Ab-initio SCF Molecular-orbital Calculations on Dinitrogen Transition-metal Complexes

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Ab-initio SCF molecular-orbital calculations have been made to test the value of such calculations by currently available procedures on the fragment $[Ru(NH_3)_5]^{2+}$ and on the species $[Ru(N_2)(NH_3)_5]^{2+}$, $[Fe(N_2)(NH_3)_5]^{2+}$, $[Ru(NH_3)_5(OH_2)]^{2+}$, $[Ru(CO)(NH_3)_5]^{2+}$, $[Mo(N_2)_2(NH_3)_4]$, $[Mo(N_2)(NH_3)_5]$, and $[Mo(N_2)_2(PH_3)_4]$. In general where direct comparisons can be made, calculation and experiment are in reasonable agreement. It is predicted that the relative polarization of bound dinitrogen changes considerably from complex to complex, with the Mo and Ru complexes being in the senses $Mo\text{–}\overset{\delta+}{N}\text{–}\overset{\delta-}{N}$ and $Ru\text{–}\overset{\delta-}{N}\text{–}\overset{\delta+}{N}$. The calculations suggest that the instability of $[Fe(N_2)(NH_3)_5]^{2+}$ compared to $[Ru(N_2)(NH_3)_5]^{2+}$ is due to the lability of the iron–ammonia system rather than to any weakness of the $Fe\text{–}N_2$ bond.

IN this paper we present the results of *ab-initio* SCF molecular-orbital (m.o.) calculations on some transition-metal dinitrogen complexes. The project should be considered as exploratory because, with the present level of computational technology, calculations of this kind are expensive and there is no guarantee that the results will be useful for interpreting experimental data.

An important feature of the types of molecule we shall consider is that their stability varies considerably with the nature of the transition metal and of the other ligands. One cannot therefore gain much insight from computationally cheap calculations on model compounds if it is known that such compounds do not show the properties which one is aiming to understand. For this reason we must at some stage tackle complexes of the second transition series with, for example, phosphine ligands, because these are the compounds whose properties are of interest to the experimentalist.

There are in practice limits to the number of atomic centres and the number of atomic orbitals that can be included in SCF programs † and these do not allow one to make calculations on all molecules that might be of interest. Thus whilst triphenylphosphine is an important stabilizing ligand for a range of dinitrogen complexes in low oxidation states it has too many atoms to be considered by *ab-initio* methods in any current program.

Semi-empirical SCF m.o. calculations are of course an alternative to *ab-initio* calculations and they have the advantage not only of cheapness but also of the ability to simulate changes of the metal and ligand by parameter modification. The weakness however is that one can choose the parameters to produce the answers that one desires. It needs to be stressed that this field is not like that of Hückel calculations on aromatic hydrocarbons where correlations can be deduced which are independent of the α and β parameters. The results of extended-Hückel or other semi-empirical calculations on transition-metal complexes are sensitive to the choice of parameters.[2] Thus whilst we would not reject such calculations, and they have been shown to be useful, they do not have the same degree of independence from the preconceived ideas of the operator as do the *ab-initio* methods.

Feasible *ab-initio* calculations on complicated molecules must also be considered as a model. They can be carried out only with small atomic orbital basis sets and they will make no allowance for specific electron correlation. It is known from calculations on small molecules that the results can be useful but have limited accuracy in respect of the energies, electron densities, and equilibrium bond lengths that are reproduced. It needs to be shown for the types of molecule in which we are interested that these model calculations are no less useful than they are on small molecules.

In calculations on molecules with heavy atoms many of the basis functions are used to represent inner shells which have little chemical importance in the sense of their involvement in the valence molecular orbitals (*i.e.* the high-energy occupied and vacant orbitals). It is possible to exclude specific consideration of inner-shell orbitals from the SCF procedure by adopting one of the pseudo-potential or model-potential methods. Most of these fall into the category of approximate *ab-initio* rather than semi-empirical methods. In other words they do not involve parameters fitted to molecular properties. We have made use of one such method which is available to us with the programs used but do not wish to imply that it is the best that could be done in this field.[3]

Minimal-basis SCF m.o. calculations on small molecules with light atoms are in general routine in that the standard computer programs which exist will converge on the ground-state wavefunction without expert intervention by the operator of the program. For large molecules, and particularly those with open shells, this is not always the case. The reason is that there is usually more than one electron configuration which is in competition for the ground-state configuration. In the SCF method the energy of an orbital depends on the distribution of electrons amongst all the orbitals and, most important, on whether that orbital contains electrons or

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† For example the program used for our calculations, ATMOL/3, has a limit of 50 atomic centres and 127 atomic basis functions.[1]

not. Suppose that the SCF procedure converges on a configuration in which the highest occupied orbital is ψ_a with energy E_a and the lowest vacant orbital is ψ_b, of different symmetry to ψ_a, with energy E_b, E_a being less than E_b but the gap $E_b - E_a$ being small. There is then the likelihood that another configuration with $\bar{\psi}_b$ occupied ($\bar{\psi}_b$ being an orbital with the same symmetry as ψ_b and approximately the same wavefunction) and $\bar{\psi}_a$ unoccupied will have a lower energy. If ψ_a and ψ_b have the same symmetry and $E_b - E_a$ is small then a single configuration will be a poor representation of the ground state.

Thus the computer program may in the first place require intervention by the operator to obtain convergence and in the second place any convergence solution will need to be tested to see whether it represents the lowest-energy configuration. Facilities for assisting convergence and for imposing orbital occupations are usually contained in the program.

RESULTS AND DISCUSSION

Compounds studied.—The compounds studied were chosen to investigate some important features of the stability of dinitrogen complexes. As we have already said this is an exploratory rather than an extensive study of each molecule and arguments could clearly be made for having chosen other compounds, and for a study of our chosen molecules in greater depth. We hope, however, that sufficient compounds have been studied to allow us to make some generalizations concerning the stability of the complexes and the comparison of dinitrogen with other ligands.*

The first dinitrogen complex to be made was $[Ru(N_2)(NH_3)_5]^{2+}$.[4] For this reason, and because of its exceptional stability, this was one of our chosen species. Experimentally it is known that the stability of complexes in the series $[RuX(NH_3)_5]^{2+}$ is in the order $X = CO > N_2 > H_2O$. Enthalpies of reaction of $N_2(g)$ and $CO(g)$ with $[Ru(NH_3)_5(OH_2)]^{2+}$ in aqueous solution are -77 ± 4 and -151 ± 7 kJ mol^{-1}, respectively.[5] Thus CO will displace both N_2 and H_2O from their complexes and N_2 will displace H_2O under normal pressure. Neither N_2 nor H_2O can displace CO.[5]

Iron is in the same periodic group as Ru but the complex $[Fe(N_2)(NH_3)_5]^{2+}$ has not so far been prepared. It is therefore of interest to study this system to see if there is any simple explanation for the difference between the two metals. Six-co-ordinated complexes of Cr, Mo, and W in zero oxidation state are isoelectronic with the Fe,Ru series. The ammine dinitrogen complex $[Mo(N_2)_2(NH_3)_4]$, is not known whereas with phosphine ligands several complexes are known.[6] We have therefore studied the three compounds $[Mo(N_2)_2(NH_3)_4]$, $[Mo(N_2)_2(PH_3)_4]$, and $[Mo(N_2)(NH_3)_5]$, the last being to allow a direct comparison with the Fe,Ru series.

There are conflicting views on the polarization of the N_2 ligand and it is by no means certain that it is in the same sense in all compounds. This point will be discussed for the compounds we have examined.

Geometries and Basis Sets.—The computational cost of the project does not allow the geometries of the complexes to be optimized by calculations so that we are restricted to a single calculation on each complex at an assumed geometry based on experimental evidence. For $[Ru(N_2)(NH_3)_5]Cl_2$ there are *X*-ray studies which have led to an estimate of the Ru–N–N distance with the other geometrical parameters being assumed.[7] There are also *X*-ray data on *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$,[8] and the N–N distance is very close to that deduced for the ruthenium complex. For the other complexes we have no direct data and assumed values have been adopted throughout. We have made the following assumptions:

(1) The bond lengths for NH_3 as a ligand are the same as in the free molecule.
(2) The NH_3 bond angles are tetrahedral.
(3) The ligand–metal bonds are in an octahedral relationship.
(4) The four NH_3 ligands which are *cis* to N_2 (or CO or H_2O) are related by a C_4 operation. In each case one NH bond lies in the equatorial (*xy*) plane.
(5) The *trans* NH_3 ligand has one NH bond eclipsing an equatorial M–N bond (lying in the *xz* plane).
(6) The M–N–N and M–C–O bonds are collinear and chosen to lie on the *z* axis.
(7) The H_2O ligand lies in the *xz* plane with free-molecule parameters.
(8) The N–N distance is equal to the experimental value for the ruthenium complex in all cases.

All other distances were based on averages from known compounds or an extrapolation from related compounds. There is a large amount of guess-work here and we would not wish to argue strongly for our choices. The selected bond lengths are given in Table 1.

TABLE 1

Distances (Å) used in the calculations

Ru–NH_3	2.10	Fe–NH_3	1.98
Ru–N_2	2.10	Fe–N_2	1.75
Ru–CO	2.00	N–N	1.12
Ru–H_2O	2.10	C–O	1.19
Mo–PH_3	2.45	N–H	1.05
Mo–N_2	2.01	P–H	1.42
Mo–NH_3	2.13	O–H	0.958

The atomic orbital basis functions are contracted gaussian functions representing minimal-basis Slater-type orbitals. For C, N, and O the 1*s* and 2*s* are three-gaussian expansions of the Clementi and Raimondi minimal Slater basis and the 2*p* orbitals are four-gaussian expansions of the Hartree–Fock free-atom orbitals.[9,10] This recipe gives rather better results than using STO-3G for all orbitals, particularly for atoms at the end of a period (*e.g.* F or O). For hydrogen, the orbital is a Slater orbital with exponent 1.2 expanded as three gaussians. For P a three-gaussian expansion of the

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* *Ab initio* SCF m.o. calculations have been made on the interaction of N_2 and CO with isolated transition-metal atoms (see H. Veillard, *Nouveau J. Chim.*, **1978**, **2**, 215). The electronic structures of such systems bear little relation to the compounds studied in this paper.

Clementi minimal basis was used but calculations were only done in the valence-electron model already referred to.[3]

To form a basis for Ru and Mo we started with atomic calculations using the Huzinaga (17*s*, 11*p*, 8*d*) gaussian basis.[11] For the coefficients of the resulting atomic orbitals we selected contractions (*i.e.* linear combinations of the full basis) such that atomic calculations in this basis gave orbital energies and total energies close to the full-basis calculations. Satisfactory contractions could be obtained by examining the coefficients of each atomic orbital in the full calculations. For example, for the 5*s* orbital of Ru the two largest coefficients were 0.636 and 0.557 for basis functions with exponents 0.101 3 and 0.036 8, respectively, and the basis functions had no weighting greater than 10^{-2} in any of the 1*s*—4*s* orbitals. We therefore chose as one contracted function (unnormalized) 0.636 1*s*(0.101 3) + 0.557 1*s* (0.036 8) and this dominated the 5*s* orbital in the contracted-basis atomic calculations. A *p* function with exponent 0.13 was added to the basis to represent the 5*p* orbital which is vacant in the ground state of the atom. The contracted basis for Ru and Mo is given in Tables 2 and 3.

TABLE 2

Contracted basis for Ru formed from the Huzinaga (17*s*, 11*p*, 8*d*) gaussian basis

$1s = 0.0027\ s_2 + 0.0137\ s_3 + 0.0530\ s_4 + 0.1571\ s_5 + 0.3286\ s_6 + 0.3934\ s_7$
$2s = 0.1180\ s_8 - 0.4906\ s_9 - 0.6090\ s_{10}$
$3s = 0.390\ s_{11} + 0.8207\ s_{12} + 0.1317\ s_{13}$
$4s = 0.9081\ s_{14} + 0.2858\ s_{15}$
$5s = 0.6360\ s_{16} + 0.5573\ s_{17}$
$2p = 0.0026\ p_1 + 0.0199\ p_2 + 0.0932\ p_3 + 0.2757\ p_4 + 0.4455\ p_5\ 0.2951\ p_6$
$3p = 0.4259\ p_7 + 0.5736\ p_8 + 0.1381\ p_9$
$4p = 0.6913\ p_{10} + 0.3093\ p_{11}$
$3d = 0.0205\ d_1 + 0.1246\ d_2 + 0.3352\ d_3 + 0.4612\ d_4 + 0.2685\ d_5$
$4d = 0.3588\ d_6 + 0.5119\ d_7 + 0.3067\ d_8$

For the Fe basis we took best-atom Slater *s* and *p* orbitals of Clementi and Raimondi expanded in three gaussians and added single primitive 4*s* and 4*p* functions with exponent 0.32 following the procedure of Veillard and co-workers.[9,12] For the 3*d* function we used the (4*d*) gaussian basis of Roos *et al.*[13] contracted to a single function for the configuration $4s^2 3d^6$.

Calculations on the Ruthenium Complexes.—Table 4 shows the orbital energies, symmetries, and Mulliken populations for the fragment $[Ru(NH_3)_5]^{2+}$. The SCF calculations converged without difficulty to a ground state with formal configuration d^6 for the metal.

All occupied valence orbitals are listed in the Table except those which are predominantly N(2*s*) of the NH_3 ligands. The inner-shell orbitals of ruthenium, 4*p* *etc.*, have energies of $-2.4\ E_h$ and lower.* The first two virtual orbitals have been listed as these correspond to the vacant 4*d* levels of the metal. The contributions of inner orbitals to the valence molecular orbitals are not listed and this accounts for the short fall from 100% in some of the orbital populations.

TABLE 3

Contracted basis for Mo formed from the Huzinaga (17*s*, 11*p*, 8*d*) gaussian bases

$1s = 0.0004\ s_1 + 0.0029\ s_2 + 0.0145\ s_3 + 0.0541\ s_4 + 0.1575\ s_5 + 0.3306\ s_8$
$2s = 0.3934\ s_7 + 0.1822\ s_8$
$3s = 0.5153\ s_9 + 0.5888\ s_{10}$
$4s = 0.4802\ s_{11} + 0.7225\ s_{12} + 0.1175\ s_{13}$
$5s = 0.8540\ s_{14} + 0.4221\ s_{15}$
$6s = 1.0\ s_{16}$
$7s = 1.0\ s_{17}$
$2p = 0.0025\ p_1 + 0.0204\ p_2 + 0.0935\ p_3 + 0.2715\ p_4 + 0.4447\ p_5 + 0.3024\ p_6$
$3p = 0.4605\ p_7 + 0.5529\ p_8 + 0.1180\ p_9$
$4p = 0.2043\ p_9 + 0.6663\ p_{10} + 0.3202\ p_{11}$
$3d = 0.0228\ d_1 + 0.1342\ d_2 + 0.3460\ d_3 + 0.4548\ d_4 + 0.2500\ d_5$
$4d = 0.3326\ d_6 + 0.5112\ d_7 + 0.3599\ d_8$

The orbitals have been classified in the C_{4v} group although the true group for our assumed geometry is C_4. In C_{4v} the *d* orbitals transform as a_1, b_1, b_2, and *e*. Note that the orbitals are either predominantly metal orbitals or predominantly ligand orbitals so that our calculations conform quite clearly to a ligand-field model in which mixing between the two sets is assumed to be small.

TABLE 4

Valence orbital energies (hartree, E_h) and atomic populations (%) for $[Ru(NH_3)_5]^{2+}$. The populations of equatorial N and H are shown collectively

		Ru			N(eq.)		N(ax).		H	
Orbital	energy	4*d*	5*s*	5*p*	2*s*	2*p*	2*s*	2*p*	eq.	ax
$2b_2$	−1.0223	4				24		38	13	21
$7e$	−1.0203	5				46		15	25	9
$13a_1$	−0.9925					63		1	36	
$8e$	−0.9874					64			36	
$1a_2$	−0.9804					62			36	
$9e$	−0.9738	5				40		24	23	13
$4b_1$	−0.9613					63			37	
$14a_1$	−0.8912	3	8		2	78		6	5	
$5b_1$	−0.8731	19			3	73			5	
$15a_1$	−0.8560	11	1	2		5	3	73	1	4
$10e$	−0.8110			7	4	84			5	
$11e$	−0.7284	94				1			2	1
$3b_2$	−0.7176	93				2			4	
$16a_1$	−0.1855	54	21	18		1	1	4	1	
$6b_1$	−0.0709	79			4	16			1	

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* E_h = Atomic unit of energy = 2 625 kJ mol^{-1}; 1 eV ≈ 1.60×10^{-19} J.

In an octahedral complex *s*, *p*, and *d* orbitals transform as different symmetry species of the O_h group. In the lower symmetry there is appreciable mixing of these orbitals which we see particularly in the population of the virtual orbital $16a_1$. In the six-co-ordinate complexes we shall see that this mixing is much less even though some of the complexes actually have higher symmetry than the penta-ammine.

TABLE 5

Valence orbital energies (hartree) and atomic populations (%) for $[Ru(N_2)(NH_3)_5]^{2+}$

		Ru			N(eq.)		N(ax.)		H		N′			N″		
Orbital	Energy	$4d$	$5s$	$5p$	$2s$	$2p$	$2s$	$2p$	eq.	ax.	$2s$	$2p_\sigma$	$2p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$
$16a_1$	−1.1592	2	1			1					41	27		23	3	
$2b_2$	−1.0180	5				28		26	15	15			7			5
$7e$	−1.0166	5				45		13	25	8			3			2
$17a_1$	−0.9909					37		7	21	4		1	13	3	4	10
$8e$	−0.9908					35		7	20	4		1	16	3	3	12
$1a_2$	−0.9701					48		5	27	3			9			8
$9e$	−0.9786					56		2	32	1			5			4
$18a_1$	−0.9703	2				12		3	6		31	18		21	35	
$10e$	−0.9632					34		18	20	10			9			9
$4b_1$	−0.9572					63		36								
$19a_1$	−0.8839	5	6			79		2	5							
$5b_1$	−0.8674	19			3	74			5							
$20a_1$	−0.8425	7	1	4		2	3	75	1	4	1	1			1	
$11e$	−0.8060			7	4	83			5							
$12e$	−0.7139	93				1			2	1						2
$3b_2$	−0.7090	94				2			4							
$13e$	−0.1914	1		2									44			52
$21a_1$	−0.0820	81			1	5	2	5							1	
$6b_1$	−0.0620	79				16			1							

It is traditional to interpret the bonding of a ligand such as CO in terms of donation from ligand σ orbitals which are a_1 in C_{4v} and acceptance by ligand antibonding π orbitals which are *e* in C_{4v}. Thus we identify $16a_1$ as the predominant σ-electron acceptor and $11e$ as the predominant π donor of the ruthenium penta-ammine. The former will be raised in energy and the latter lowered in energy by these interactions and hence we expect that the $a_1 - e$ energy gap will be a useful measure of the total σ- and π-bonding strength. There are other factors which influence these orbital energies such as the net charge on the metal, but these should be in the same direction for both a_1 and *e* orbitals.

TABLE 6

Valence orbital energies (hartree) and atomic populations (%) for $[Ru(CO)(NH_3)_5]^{2+}$

		Ru			N(eq.)		N(ax.)		H		C			O		
Orbital	Energy	$4d$	$5s$	$5p$	$2s$	$2p$	$2s$	$2p$	eq.	ax.	$2s$	$2p_\sigma$	$2p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$
$11e$	−0.8143			7	4	83			5							1
$12e$	−0.7292	90				2		1	2	1			1			4
$3b_2$	−0.7243	93				2			4							
$13e$	−0.2013	3		3	1				1				66			26
$21a_1$	−0.0900	73	2		3	6	1	5	1		7				2	
$6b_1$	−0.0778	78			4	16			1							

Tables 5 and 6 show the valence orbitals for the ruthenium penta-ammine dinitrogen and carbonyl complexes. The pattern is very similar for both and has an obvious relationship to the orbital pattern of the free ruthenium penta-ammine. The two highest cccupied orbitals are *e* and b_2, in the same order as in the free penta-ammine, and the lowest vacant orbitals with *d* character are a_1 and b_1. However, in both cases the first virtual orbital has *e* symmetry and corresponds to the π* orbital of the new ligand.

The π and σ bonding to N_2 and CO does not lead to appreciable populations of ligand orbitals in orbitals $12e$ and $21a_1$. Indeed the ligand populations we find are surprisingly small in both although they do indicate that CO is both a better π acceptor and σ donor than N_2 which conforms with inferences made from spectral data.[6] The highest occupied orbital $3b_2$ is non-bonding to N_2 (or CO) and its energy is very close to its value in the penta-ammine fragment.

The CO complex is known to be more difficult to oxidize than the N_2 complex and this is consistent with our finding that the $3b_2$ orbital has a lower energy in the CO complex. This can be attributed to the slightly greater positive charge carried on the ruthenium atom Figure 1 shows the net atom charges which are obtained by accumulating the Mulliken populations.

Both the N_2 and CO ligands carry small charges, but the main feature is the polarization of the ligand. In the N_2 complex the terminal atom carries a positive charge and this is consistent with the fact that in this complex, which is prepared in acid solution, the N_2 is not attacked by proton acids.

ESCA measurements on dinitrogen complexes sometimes show significant differences in N(1*s*) chemical shift between the two nitrogen atoms and sometimes do not.[6,14] In cases where they do, the terminal nitrogen is usually assumed to be negatively charged. We shall see later for the Mo complex that a negative charge is predicted by calculations.

The reported ESCA spectrum of $[Ru(N_2)(NH_3)_5]^{2+}$ shows a single broad peak for N(1*s*) binding energies with no resolution of individual nitrogen atoms,[15] so our prediction of a positive terminal nitrogen has, as yet, no experimental verification.

A Mulliken population analysis can occasionally misrepresent an electron distribution if the basis consists of orbitals of very different size. To show that this is not the case for the ruthenium dinitrogen complex we show in Figure 1 the electron-difference map between the complex and the two components, $[Ru(NH_3)_5]^{2+}$ and N_2, taken with the same geometries as in the complex. The polarization of the dinitrogen ligand agrees with that inferred from the population analysis (see Figure 2).

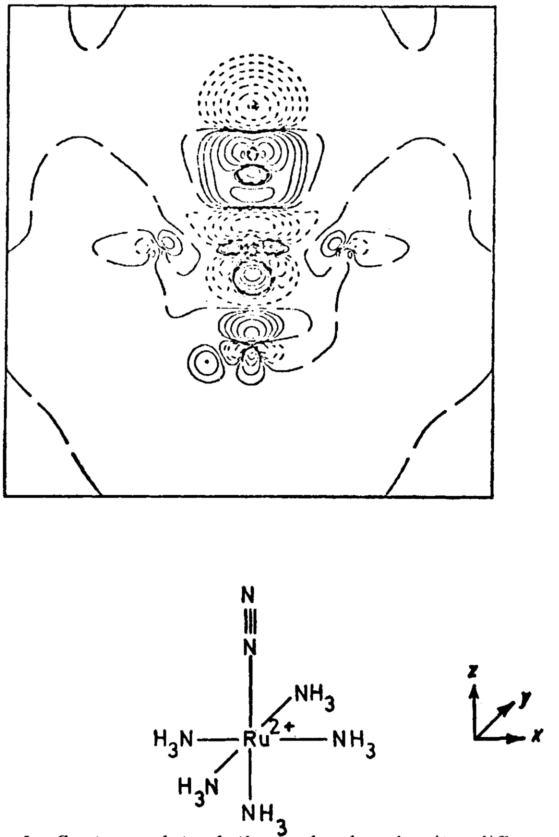

FIGURE 1 Contour plot of the molecular density difference function of $[Ru(N_2)(NH_3)_5]^{2+} - [Ru(NH_3)_5]^{2+} - N_2$. The long dashes indicate nodal lines, the solid lines positive contours, and the dashed lines negative contours

The polarization of the CO ligand is in the same sense as in the free CO but reduced slightly. We note however that the SCF procedure gives an incorrect sign for the dipole moment of CO and hence the trend we calculate may be correct but the absolute charges are probably not.

Figure 3 shows an orbital-interaction diagram for the N_2 complex which summarizes the results of the calculations. The bonding a_1 orbital which is closest in character to the highest filled free-ligand σ orbital is $18a_1$ and this has been shown in the Figure. We note however from Tables 5 and 6 that there are higher occupied a_1 orbitals which are associated with the NH_3 ligands. Dubois and Hoffmann [16] have postulated a similar interaction scheme based on semi-empirical calculations. The main difference between the two is that in our scheme

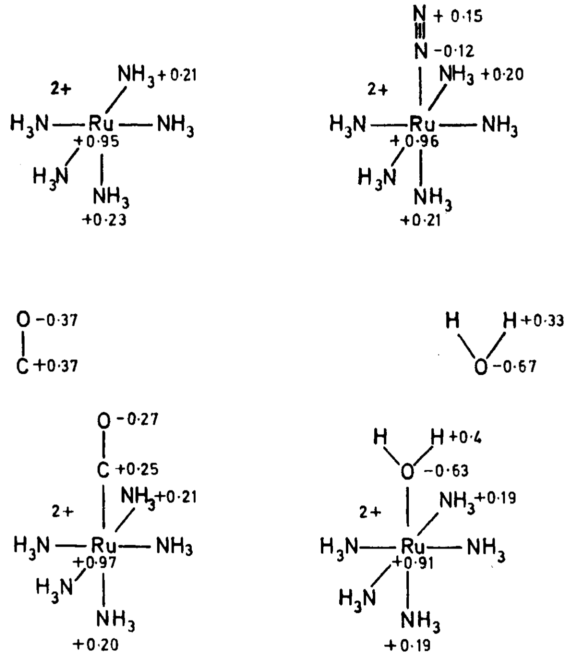

FIGURE 2 Net atom charges obtained by accumulating the Mulliken populations for the ruthenium(II) complexes

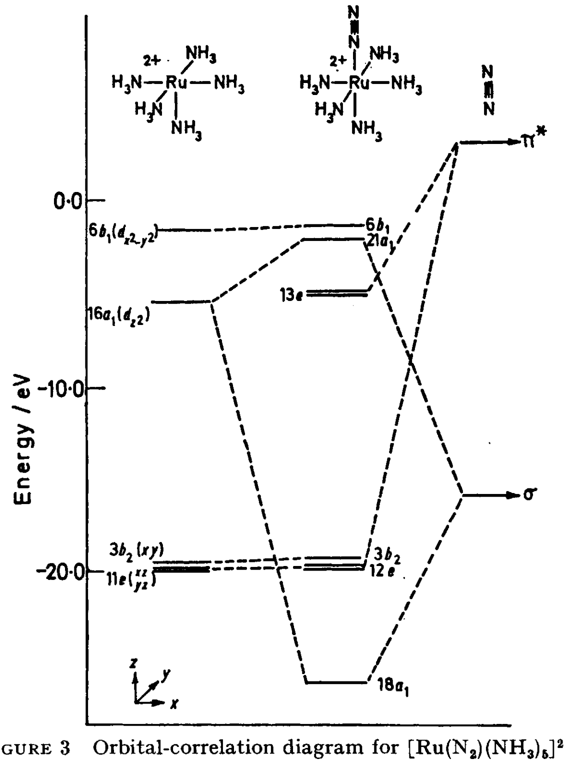

FIGURE 3 Orbital-correlation diagram for $[Ru(N_2)(NH_3)_5]^{2+}$

the virtual 13*e* orbital is appreciably stabilized by the net positive charge on the complex.

The lowest-energy excited state should be associated with the transition $3b_2 \rightarrow 13e$ and this would give a symmetry-forbidden metal-to-ligand charge-transfer band. The orbital energy differences are practically identical for the N_2 and CO complexes and although we have not calculated excitation energies our conclusion is that the charge-transfer bands, which are typically broad, would be weak and not be very different in energy. This is confirmed by experiment; both complexes are yellow and show bands in the region of 200—300 μm, the dinitrogen complex shows a broad band at 221 μm,[17] and the carbonyl shows a maximum between 274 and 290 μm.[18]

TABLE 7

Valence orbital energies (hartree) and atomic populations (%) for $[Ru(NH_3)_5(OH_2)]^{2+}$

		Ru			N(eq.)		N(ax.)		H		O				
Orbital	Energy	4*d*	5*s*	5*p*	2*s*	2*p*	2*s*	2*p*	eq.	ax.	2*s*	$2p_x$	$2p_y$	H^1	H^2
10*e*	−0.7913			6	4	84			5				1		
	−0.7815			6	4	83			5						
11*e*	−0.6804	95				1			2						
	−0.6733	93				1			2				3		
$4b_2$	−0.6763	94				2			4						
$19a_1$	−0.0512	70	7	1		3	2	5	1		3	1		3	3
$5b_2$	−0.0283	80			4	15			1						

Table 7 and Figure 2 show the results for $[Ru(NH_3)_5(OH_2)]^{2+}$. This complex has a lower symmetry than the N_2 and CO complexes, and the orbitals which are *e* in C_{4v} are split. However, in all cases this splitting is small (at most 0.01 E_h) and the orbitals have therefore still been classified under C_{4v} in order to facilitate comparison with Tables 5 and 6.

As there is no low-energy orbital of π symmetry in H_2O the first virtual orbital of the complex is a_1 as in the free penta-ammine. This orbital shows more evidence of metal–ligand interaction than does the corresponding orbital $21a_1$ of the CO and N_2 complexes which is in accord with the established view that H_2O is a stronger σ donor than either CO or N_2. Figure 2 shows that the metal has a smaller postive charge in the H_2O complex.

The lowest-energy excited states would be *d–d* transitions which are generally sharper and weaker than charge-transfer bands. However the low symmetry of the complex will make the $e \rightarrow a_1$ transition symmetry allowed.

The total energies of all molecules reported in this paper are given in Table 8. Binding energies of the three complexes we are discussing can be calculated by subtraction. This makes no allowance for differences of correlation energy but should be a good guide to the relative stabilities of the complexes.

The calculations predict an order of stability $H_2O >$ CO $> N_2$, the stabilization energies of the appropriate penta-ammine complexes being 144, 108, and 86 kJ mol^{-1}, respectively. The CO,N_2 order is as deduced from experiment but the position of H_2O is not in agreement with experiment. However, it must be remembered that the experimental results are for aqueous solutions not for the gas phase and we must therefore take account of the binding energy of the displaced water molecule with bulk water. The enthalpy of vaporization of water is 45 kJ mol^{-1} at 273 K, so that a value of this order of magnitude subtracted from the calculated binding energy would not be inappropriate,[19] as the solvation energy of water bound in the complex should be low.

Calculations on Complexes of Fe *and* Mo.—Tables 9—11 give the results of calculations on some complexes of Fe and Mo and Figure 4 summarizes the predicted charge distribution. Our first comparison is between the iron dinitrogen complex and the ruthenium dinitrogen complex already discussed.

There are very few differences in the orbital patterns for the iron and ruthenium complexes, both the energies and atomic populations being very close. The largest difference is found in orbital $5b_1$ which shows much less mixing of metal and ammonia orbitals in the iron complex than in the ruthenium complex. It is this, shown to a lesser extent in $19a_1$ and $20a_1$, that leads to a much larger positive charge on the metal and smaller charges on the ammonia ligands. The net charge on the N_2 ligands and its polarization are not very different in the two complexes. Our conclusion is that there is nothing in these results which points to the iron–dinitrogen bond being less strong than the ruthenium–dinitrogen bond, although the iron complex has not been prepared. This negative result must be seen in the light of the fact that iron(II) ammines are very labile and penta-ammines or hexa-ammines are difficult to isolate. We conclude that the failure as yet to obtain such an

TABLE 8

Total SCF energies (hartree) for the compounds studied

	State configuration	Energy
$[Ru(NH_3)_5]^{2+}$	$^1A_1(e^4b_2^2)$	−4 694.1988
$[Ru(N_2)(NH_3)_5]^{2+}$	$^1A_1(e^4b_2^2)$	−4 801.8614
$[Ru(CO)(NH_3)_5]^{2+}$	$^1A_1(e^4b_2^2)$	−4 805.6558
$[Ru(NH_3)_5(OH_2)]^{2+}$	$^1A_1(e^4b_2^2)$	−4 769.4716
$[Mo(N_2)(NH_3)_5]$	$^1A_1(e^4b_2^2)$	−4 359.7138
$[Mo(N_2)(NH_3)_5]^+$	$^2E(e^3b_2^2)$	−4 359.7728
$[Mo(N_2)(NH_3)_5]^+$	$^2B_2(e^4b_2^1)$	−4 359.7930
$[Mo(N_2)_2(NH_3)_4]$	$^1A_1(e^4b_2^2)$	−4 411.8759
$[Mo(N_2)_2(PH_3)_4]$	$^1A_1(e^4b_2^2)$	−4 223.6828
$[Fe(N_2)(NH_3)_5]^{2+}$	$^1A_1(e^4b_2^2)$	−1 636.6772
N_2	$^1\Sigma_g^+$	−107.6300
CO	$^1\Sigma_y^+$	−111.4158
H_2O	$^1A_1$	−75.2181

iron(II) dinitrogen complex is due to the instability of the ligand structure. Iron is different from Ru, not in respect of the metal–dinitrogen bond but in respect of the metal–ammine bond.

The orbital energies for the neutral molybdenum com-

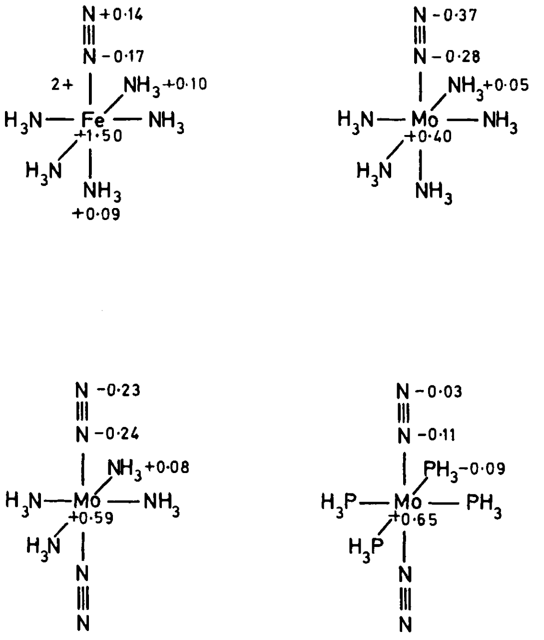

FIGURE 4 Net atom charges obtained by accumlating the Mulliken populations for the iron(II) and molybdenum(0) complexes

plexes are of course less negative than those of the complexes of Fe^{II} and Ru^{II}. The energy of the highest occupied orbital of $[Mo(N_2)(NH_3)_5]$ is in fact just positive and that of the second occupied orbital only just negative. This complex is not known and the calculations suggest that it is unlikely to be stable. Calculations have also been made on the + 1 oxidation state and the $^2B_2$ $(e^4b_2^1)$ state is predicted to be more stable than the ^2E $(e^3b_2^2)$ by 0.02 E_h, contrary to the orbital sequence obtained for the neutral compound.

The orbital pattern for $[Mo(N_2)_2(NH_3)_4]$ suggests that this is more stable than $[Mo(N_2)(NH_3)_5]$ as all occupied orbitals have negative energies. The highest occupied orbital $4e_g$ shows substantial d–π mixing in comparison with the ruthenium complex. As for the mono(dinitrogen) complex there is no low-lying σ-acceptor orbital on the metal so that in these complexes the dinitrogen ligand is behaving predominantly as a π acceptor and consequently carries a substantial negative charge.

Calculations on the molybdenum phosphine complex were made in a valence-electron approximation described elsewhere.[3] It would have been feasible to treat all inner shells by a core approximation but to give maximum comparison with the ammine complex it was decided to treat the metal core electrons and the dinitrogen core electrons explicitly so that only the phosphorus inner shells were involved in the approximation. Other phosphorus compounds have been treated satisfactorily using the valence-electron model.[20] We encountered difficulty in obtaining convergence of the SCF calculations for the phosphine complex. This is almost certainly due to the presence of low-energy virtual orbitals, particularly the vacant orbital $16a_{1g}$ at −0.19 E_h. A single cycle of the SCF iteration took 20 s on an IBM 360/195 and the calculations were stopped after 24 cycles when the convergence test criterion (which is a measure of the largest off-diagonal element of the Fock matrix) was 10^{-2}. Other calculations reported in this paper converge to 10^{-3} after this number of cycles.

A comparison of Tables 11 and 12 shows that the phosphine ligands stabilize the orbital energies in comparison with the ammine ligands. The highest occupied orbital has an energy of −0.30 E_h which corresponds to an ionization potential of 8 eV.

TABLE 9

Valence orbital energies (hartree) and atomic populations (%) for $[Fe(N_2)(NH_3)_5]^{2+}$

		Fe			NH_3			N′			N″		
Orbital	Energy	$3d$	$4s$	$4p$	$2s$(N)	$2p$(N)	$1s$(H)	$2s$	$2p_\sigma$	$2p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$
$16a_1$	−1.2159	2					3	41	35		17	1	
$7e$	−1.0527	6				23	12			36			23
$2b_2$	−1.0354	5				61	34						
$8e$	−1.0158					45	25		1	10	3	5	8
$17a_1$	−1.0147					27	15		7	3	20	25	3
$18a_1$	−0.9927					49	25	1	6		7	11	
$9e$	−0.9893					57	33			4			5
$4b_1$	−0.9831					61	37			1			1
$10e$	−0.9620					59	35			3			3
$1a_2$	−0.9561					62	38						
$19a_1$	−0.9057	2	2		2	83	6	2	1			1	
$5b_1$	−0.8423	8			4	83	5						
$20a_1$	−0.8410	4		1	4	84	6						
$11e$	−0.8373			3	4	85	6						1
$3b_2$	−0.7845	95				2	3						
$12e$	−0.7803	92				1	3						4
$13e$	−0.2049	2								44			53
$6b_1$	−0.0830	92			2	6							
$21a_1$	−0.0830	84			3	4	5	3				1	

The phosphine ligands are predicted to carry net negative charges (Figure 4) and this results in a decrease in the negative charge carried on the dinitrogen ligands. The phosphine ligands behave as electron acceptors as shown by their influence on the lowest vacant orbitals in the complex.

TABLE 10

Valence orbital energies (hartree) and atomic populations (%) for $[Mo(N_2)(NH_3)_5]$

		Mo			N(eq.)		N(ax.)		H		N′			N″		
Orbital	Energy	$4d$	$5s$	$5p$	$2s$	$2p$	$2s$	$2p$	eq.	ax.	$2s$	$2p_\sigma$	$2p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$
$11e$	−0.4142			4	7	80			3				2			3
$20a_1$	−0.3919	1	1	2				4			4	24		21	41	
$3b_2$	−0.0021	95							5							
$12e$	0.0181	76							2	1			5			17
$21a_1$	0.3398		4	1	13		5		24	12						
$13e$	0.3767	17		6	1				2	1			36			36
$22a_1$	0.5109	2	1	5	8	4	11	3	28	36						

It is known that *trans*-$[Mo(N_2)_2(PR_3)_4]$ (PR_3 = tertiary phosphine) react with proton acids under mild conditions to yield hydrazine and ammonia. There is strong presumptive evidence that these reactions involve proton attack on a nitrogen remote from the metal as a first step.[6] This is consistent with the negative charge inferred from the calculations.

TABLE 11

Valence orbital energies (hartree) and atomic populations (%) for $[Mo(N_2)_2(NH_3)_4]$

		Mo			NH$_3$			N′			N″		
Orbital	Energy	$4d$	$5s$	$5p$	$2a$(N)	$2p$(N)	$1s$(H)	$2s$	$2p_\sigma$	$2p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$
$3b_{1g}$	−0.4964	11			5	80	4						
$7e_u$	−0.4534			5	6	83	4						1
$3b_{2g}$	−0.0934	96					4						
$4e_g$	−0.0754	67					2			7			24
$8e_u$	0.2129			5			1			42			51
$16a_{1g}$	0.3337	1	50		12		32						
$5e_g$	0.3344	28					1			38			33

There has been some controversy over the order of the highest orbitals in complexes of this type, albeit with more complicated phosphine ligands. Dubois and Hoffmann[16] on the basis of a semi-empirical m.o. scheme suggested that b_{2g} was the highest occupied orbital with e_u below that and the lowest vacant orbital was e_g. Chatt *et al.*[21] suggested that the highest occupied orbital should be e_g, as this has metal–N_2 bonding character (the b_{2g} has no contribution from N_2 orbitals by symmetry).

TABLE 12

Valence orbital energies (hartree) and atomic populations (%) for $[Mo(N_2)_2(Ph_3)_4]$

		Mo			PH$_3$			N′			N″		
Orbital	Energy	$4d$	$5s$	$5p$	$3s$(P)	$3p$(P)	$1s$(H)	$2s$	$2p_\sigma$	$2p_\pi$	$2s$	$2p_\sigma$	$2p_\pi$
$7e_u$	−0.5461			13	−6	36	56						1
$1a_{2g}$	−0.5333					49	51						
$3b_{1g}$	−0.4495	4			11	40	45						
$3b_{2g}$	−0.3295	85					15						
$4e_g$	−0.3002	77					8			6			7
$16a_{1g}$	−0.1922	12	78		−8	48	1						
$8e_u$	−0.0474			55	−8	33	11			2			4
$4b_{1g}$	−0.0239	48			−1	19	34						

This is reflected by the facts that loss of a dinitrogen ligand is accelerated by irradiation with visible light and that loss of dinitrogen is the initial step in the decomposition of $[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]^+$.[21]

Our calculation supports the suggestion of Chatt *et al.* although the b_{2g} — e_g gap is not large (see Table 12). We predict that the lowest vacant orbital is a_{1g}, whereas both Dubois and Hoffmann and Chatt *et al.* suggest that it is e_u, which in our calculations is the second virtual level.

Chatt *et al.*[21] argue on the basis of the appearance of a charge-transfer band for the complex $[Mo(N_2)_2(dppe)_2]$ at *ca.* 26 000 cm^{-1} that the energy gap between the highest occupied and lowest vacant orbital predicted by Dubois and Hoffmann[16] is too low. Our separation (*ca.* 3 eV) is substantially higher and although we have not calculated the energy of the first excited state it should not be inconsistent with the observed spectrum. From our calculations the first electronic transition should be metal-to-phosphine charge transfer which contrasts with the prediction of Dubois and Hoffmann, and of Chatt *et al.* It is not clear that this charge transfer has any relevance to the reduction of the dinitrogen. However, the valence-electron model we used has been found to be less accurate for virtual orbitals than for occupied orbitals so we treat our inference with some reservation.

Where we can make comparisons of our inferences with experiment there is reasonable agreement. This gives us some confidence in the predictions which cannot as yet be checked empirically, such as the polarity of co-ordinated dinitrogen, or the stability of $[Fe(N_2)(NH_3)_5]^{2+}$, which we shall now attempt to isolate. It would be of great value to be able to investigate the consequences of changing geometries. This would enable us to discuss mechanisms with some confidence, but it would go beyond the current SCF limit. These types of calculation have not yet reached the routine level where they are open to the preparative chemist *via* the widely available *ab-initio* programs.

[9/1426 *Received, 6th September,* 1979]

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