dipole moment of propynal (2.74 D[32] compared with the previous value of 2.46 D[33]).

Conclusions

Several important points emerge from this study.

(1) Propadienone, propynal, and cyclopropenone have comparable energies but in the order propynal < propadienone < cyclopropenone.

(2) Propadienone is predicted (6-31G**) to have an equilibrium structure which is planar with C_{2v} symmetry but to possess low-frequency vibrations of b_1 and b_2 symmetry which allow easy distortion from such a structure. This may be responsible for the apparent disagreement between theoretically calculated and experimentally observed properties (e.g., rotational constants, dipole moment) for propadienone.

(3) Propadienone can dissociate to vinylidene plus carbon monoxide via a transition state resembling a weak complex of the products in an endothermic reaction requiring about 32 kcal mol^{-1} activation energy. Subsequent rearrangement of vinylidene to acetylene leads to an exothermic dissociation plus rearrangement reaction.

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Hexaammineruthenium(II,III) and Pentaamminedinitrogenruthenium(II). A Hartree–Fock–Slater Study

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Abstract: Discrete variation method Hartree–Fock–Slater studies are reported for the title compounds. The significant σ covalency and strong π back-bonding in the dinitrogen complex are apparent from populations, energy shifts, optical spectra, and reorganization effects on optical excitation; the energy levels are strongly perturbed by the strong covalency from their pseudooctahedral crystal field values. Transition-state calculations yield optical and photoemission results in good agreement with experiments. In the dinitrogen compound, the directly bonded N is considerably more negative, in agreement with simple electrostatic and bonding arguments.

The rich redox chemistry of Ru^{II} and Ru^{III} complexes has been carefully elucidated, particularly in the early probing and elegant work of Taube and his students.[1-3] In particular, the strong π-back-bonding ability of Ru has been demonstrated in a series of chemical and physical studies. One of the most striking evidences of the π-base strength of Ru is the easy preparation and marked stability of the $(NH_3)_5Ru^{II}(N_2)$ (I) complex, which was one[4] of the first stable dinitrogen metal complexes to be prepared; the N_2 ligand will[5] actually displace water from the aquopentaammineruthenium(II). The properties of I have been widely interpreted[3] as arising from the strength of its π back-bonding. Comparison with the $(NH_3)_6Ru^{II}$ (II) complex, which contains the same primary coordination sphere but cannot support π back-donation, should be particularly helpful in clarifying the role of this interaction. More recently, attention has been focused[6-13] on the intramolecular electron-transfer properties of binuclear complexes containing the $(NH_3)_5Ru^{II}$ L species, where L is a π-acceptor ligand (N_2, pyrazine, 4,4′-bipyridyl, cyanogen, etc.).

Table I. Internuclear Distances (μ_β)[a]

II		I		III	
$Ru(NH_3)_6{}^{2+}$		$(NH_3)_5RuN_2{}^{2+}$		$Ru(NH_3)_6{}^{3+}$	
Ru–N	4.052	Ru–N(eq)	4.014	Ru–N	3.976
N–H	1.907	Ru–N(ax)	4.044	N–H	1.907
H–H	3.048	Ru–N	3.645	H–H	3.048
		N–N	1.124		
		N–H	1.907		
		H–H	3.048		

[a] Taken from ref 26 and 21. The Ru–N–N group is from the dimer and probably overstates the Ru–N distance; see text.

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Table II

II	I	III
	Ground-State Molecular Orbitals and Populations	
	$41a_1$ (−9.23 eV) (100% NH_3)	
$11a_{1g}$ (−8.38 eV)	40_1 (−11.61 eV) (30% 4d) (52% N p_σ)	$11a_{1g}$ (−13.41 eV)
$9e_g$ (−8.65 eV)	$39a_1$ (−11.61 eV) (35% 4d) (34% N p_σ)	$9e_g$ (−15.51 eV)
$10a_{1g}$ (−11.81 eV)	$17a_2$ (−11.69 eV) (11% 4d) (86% N $p\pi$)	$10a_{1g}$ (−19.27 eV)
$8e_g$ (−11.89 eV)	$38a_1$ (−11.93 eV) (62% 4d) (37% NH_3)	$8e_g$ (−19.32 eV)
$8e_u$ (−18.30 eV)	$16a_2$ (−15.19 eV) (92% 4d) (8% NH_3)	$8e_u$ (−23.95 eV)
	$37a_1$ (−15.46 eV) (81% 4d) (13% $2p\pi$)	
	$15a_2$ (−15.43 eV) (81% 4d) (13% $2p\pi$)	
	Total Valence Population	
Ru s 2.00	Ru s 1.88	Ru s 1.99
Ru p 6.12 $Ru^{1.39}$	Ru p 5.59 $Ru^{2.09}$	Ru p 6.13 $Ru^{1.89}$
Ru d 6.49	Ru d 6.42	Ru d 5.98
N s 1.86 N p 2.85 $N^{1.71-}$	N^{near} s 1.58 N^{near} p 3.80 $N^{0.48-}$	N s 1.88 $N^{1.78-}$ N p 4.91
H s 0.40 $H^{0.60}$	N^{far} s 1.71 N^{far} p 3.08 $N^{0.21}$	H s 0.34 $H^{0.66}$
	N^{ax} s 1.80 N^{ax} p 4.64 $N^{1.45-}$	
	N^{eq} s 1.78 N^{eq} p 4.71 $N^{1.48-}$	
	H s 0.50 $H^{0.50}$	

Attempts to understand the bridge-assisted, inner-sphere intramolecular electron-transfer rates in these systems require knowledge of the electronic structure, particularly[10–13] the effective electronic matrix elements between localized (largely the Ru orbital) sites on the left and right sides of the binuclear complex. Several theoretical models[10–13] have been put forward to understand this electron-transfer event, but, so far as we have been able to ascertain, no quantitative, first-principle, nonempirical data have been obtained to characterize the extent of orbital mixing and delocalization in these systems. Some important semiempirical work has been reported,[10–14] in particular with regard to oxidative addition reactions and to the extent of bridge-induced valence mixing.

We report here first-principle Hartree–Fock–Slater discrete variation method (HFS-DVM)[15] studies on I, II, and $(NH_3)_6Ru^{III}$ (III). These studies indeed indicate strong π back-donation with the π-acceptor ligand of I. In addition, they confirm the assignments[3,16] of the optical spectra of I and appear to resolve some discrepancies in assignment[17] of the optical spectra of II and III. Finally, they seem to indicate that the strength of the π interactions, at least for the N_2 ligand, militates against a simple atom-localized orbital to describe the transfer site in binuclear complexes and strongly suggests a Robin–Day[18] III classification (delocalized) for well-conjugated ligands with good π-acceptor properties.

Calculations

Geometric data used in the calculations are summarized in Table I. For purposes of the present calculation, NH_3 ligands were rotated so that the ions II and III have D_{3d} symmetry; the symmetry of I is C_s.

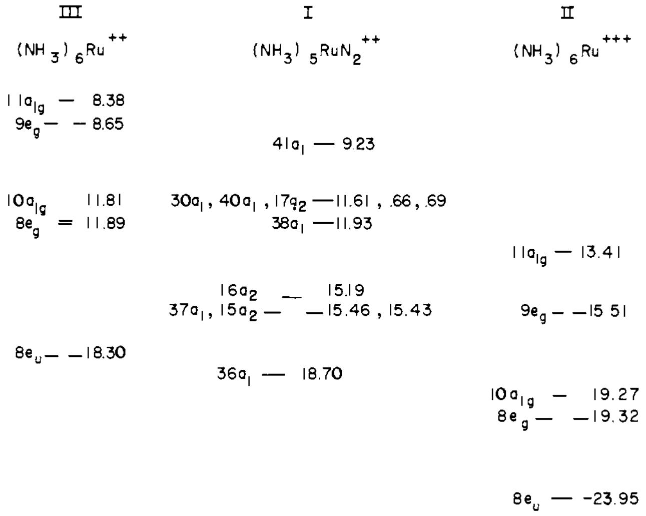

Figure 1. Calculated orbital energies: I = $(NH_3)_5RuN_2^{2+}$; II, $(NH_3)_6Ru^{2+}$; III, $(NH_3)_6Ru^{3+}$. Note that all orbital energies are negative.

Numerical minimum basis sets were used for N and H, while 5s and 5p functions were included for the Ru atoms. For improvement of the basis sets, self-consistency was attained in the HFS-DVM molecular calculation, then the resulting Mulliken populations were used to calculate better atomic basis functions.[15] This process was performed only once for N and H but was repeated many times for Ru, to obtain a high-quality Ru basis set. Ionization potentials (IP's) and energies of optical transitions were calculated by a transition operator method.[19] This procedure contains only one free parameter, the exchange/correlation factor X_α (taken as 0.7 here); it should yield an accurate and unbiased description of the electronic structure of these complexes.

Results

A. Ground States. Ground-state molecular orbitals near the Fermi level, with their corresponding eigenvalues, are shown in

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Table III. Variation of $(NH_3)_5RuN_2{}^{2+}$ Molecular Orbital Energies with Ru–N_2 Distance

$x_{\text{Ru-N}}$ = 6.176 Å	$x_{\text{Ru-N}}$ = 1.928 Å	$x_{\text{Ru-N}}$ = 1.716 Å	
8.84	10.29	10.73	$17a_2$
8.84	10.20	10.66	$40a_1$
10.99	10.24	10.77	$39a_1$
12.77	10.44	11.77	$38a_1$
14.18	13.87	15.06	$16a_2$
14.22	14.17	15.32	$15a_2$
14.19	14.15	15.29	$37a_1$
$Ru^{1.93}$	$Ru^{1.69}$	$Ru^{2.12}$	

Table II and in Figure 1. Note for II and III that the presence of the H atoms has caused a lowering of symmetry, such that the set of five orbitals which consist primarily of Ru 4d functions are ($8e_{g1}$, $8e_{g2}$, $10a_{1g}$; $9e_{g1}$, $9e_{g2}$) instead of the usual (t_{2g}; e_g); here the 1 and 2 denote the individual partners in the e_g representation. However, one can see that the set ($8e_{g1}$, $8e_{g2}$, $10a_{1g}$) is nearly degenerate, with an energy difference of about 0.08 eV for the II and about 0.06 eV for III. The Fermi energy cuts, as expected from simple crystal field arguments, between MO's consisting largely of Ru (d_{xy}, d_{xz}, d_{yz}) and MO's containing principally Ru ($d_{x^2-y^2}$, d_{z^2}). Very roughly, III has an energy level structure quite similar to that of II, but with the levels all dropped by about 7 eV due to the higher formal charge.

Closer examination reveals significant differences between II and III. In particular, the energy difference between the Ru e_g orbitals and the ammonia lone pairs decreases from 9.7 to 8.4 eV as the charge increases, leading to more σ occupancy on the metal and stronger σ bonds (which imply, as observed, a higher symmetric M–$(NH_3)_6$ stretch frequency). This is apparent in the total and orbital Mulliken populations listed in Table II. We see here that, in accord with the Pauling electroneutrality principle, the formal charges on the metal in II and III are reduced to 1.386 and 1.893, respectively. The d population in II, however, is 6.49 rather than the crystal field value of 6.00, due to σ acceptance. This effect is more pronounced, as expected from the orbital energies, in III, where the σ acceptance by the Ru is greater, and the difference between calculated and crystal field d populations is 0.98 electron. A second difference between II and III is the decrease in the gap between the metal $d\pi$ orbitals and the ammonia lone pairs upon loss of (formally) one $d\pi$ electron. This is easily understood on an electrostatic basis. The ionized electron was principally in the $d\pi$ orbitals, so they are stabilized more (lose more electron repulsion) than the ammonia orbitals. Indeed the populations of Table II show that the major change in charge is solely in the metal d's; there is a good deal of charge coming out of the ammonias (0.49 electron), but each N or H changes little.

The calculations of I are slightly complicated by lack of geometrical data. Crystals containing I are disordered,[20] and no precise data are therefore available. The N_2-bridged species $[(NH_3)_5RuN]_2{}^{4+}$ has been studied;[21] the Ru–N distances there are 2.14 and 2.12 Å for the axial and equitorial ammonias and 1.928 Å to the bridge nitrogen; the N–N distance is 1.124 Å. One expects, however, that the Ru will be of higher effective positive charge in the mononuclear than in the binuclear complex because of more significant back-bonding; this should decrease the Ru–N distance. This same suggestion has been made by Kettle and co-workers[22] on the basis of the vibrational spectrum; in the azido species, the Ru–N changes from 1.93 to 1.89 Å. We have therefore performed calculations for several choices of the Ru–N distance and find that the results are quite sensitive to this geometric parameter (as must be expected for a strong σ- and π-bonding situation). We will describe first the results for the putative geometry, with the 1.876-Å Ru–N bond.

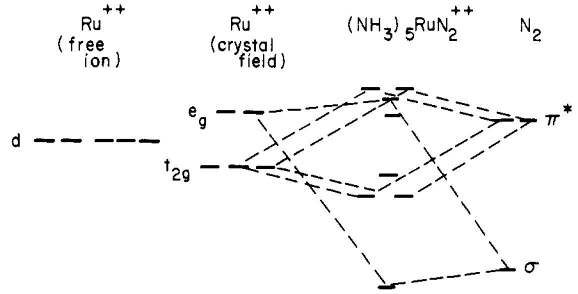

Figure 2. Schematic molecular orbital splitting diagram. The N_2 orbitals have been shifted down from their free-molecule values in view of the 2+ charge.

Upon exchange of an NH_3 for N_2, π back-bonding becomes available and the electronic structure changes considerably; qualitatively, the changes are described by the MO splitting diagram of Figure 2. Table III and Figure 1 show that the Ru$(NH_3)_5$ moiety in I is partially between that in III and that in II. This is most apparent in the HOMO energy but is also clear in the charge distribution on the ammonias. Most striking is the strong splitting in the Ru t_{2g} levels, with the two which can stabilize by back-donation (the dominant components of $37a_1$, $15a_2$) being stabilized by this covalent interaction by 0.3 eV, compared with the non-back-bonding, nearly pure Ru d level $16a_2$. The analogous splitting is only 30% as big in II. The gap at the Fermi level is essentially the same in I as it was in II, largely because the relevant LUMO ($38a_1$) and HOMO ($16a_2$) levels are nearly pure Ru σ, with a small admixture of ammonia and essentially no dinitrogen contribution. The populations show the back-bonding very clearly: The Ru d and the ammonia populations are sensibly the same as in II, but the metal charge is 0.7 unit higher, due to the outflow of $d\pi$ density onto N_2. The gross charge on the N_2 (−0.27) is in keeping with estimates from ESCA work[23] and previous[14] semiempirical calculations; the observed decrease in N_2 stretch frequency from 2330 cm^{-1} in the free ligand to 2100–2170 cm^{-1} in the complex mirrors the weakening of the N_2 bond by the acceptance. The strong imbalance of charge on the N_2 is an interesting result, since the charge polarity on the N_2 has been a point of some contention.[14] We find the more negative N atom to be the one directly bonded to the metal; this is in agreement with arguments based on the vibrational spectrum[23] but in disagreement with good semiempirical calculations on analogous model species.[14] Nevertheless, we feel that this picture, which arises from stronger back-bonding in the closer N, is a reasonable one.

The high positive charge on the Ru should polarize the N_2 in the fashion suggested by our calculation; the allyl analogy used previously[14] may be deceptive, since the extent of mixing of the N_2 π with the Ru is quite small (probably because of the large energy difference); the N_2 π^* does mix, but then the allyl analogy (Ru–N–N as the three carbons) would involve only the lowest MO of allyl and would indeed predict the negative charge to be at the near (Ru-bonded) N. This point is not susceptible to proof by density difference crystallography due to disorder[20] but might be investigated by ^{15}N NMR techniques.

Taube has stressed[3] the synergic nature of the π back-donation and the σ donation; our calculations show that both are strong enough that the crystal field picture based on pseudooctahedral symmetry is a very poor starting point for assignment of the spectra or chemical properties. This covalency is very apparent in the energy level diagrams of Figure 1. While our calculated crystal field splitting Δ of 25 900 cm^{-1} for II is in excellent agreement with the ligand field value of 27 100 given[24] by Schmidtke, there is little relation to the diagram for I, where the covalency leads

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Table IV. Energy of HOMO → LUMO Transition in Ruthenium Hexaammines

compd	$\Delta E(t_{2g} \rightarrow e_g)$,[a] eV calcd	$\Delta E(t_{2g} \rightarrow e_g)$,[a] eV exptl	ϵ, m^{-1} cm^{-1}
$[Ru(NH_3)_6]^{2+}$	3.24	3.22[b]	39[b]
		3.10[c]	30[c]
$[Ru(NH_3)_6]^{3+}$	3.82	3.87[c]	100[c]

[a] The $t_{2g} \rightarrow e_g$ transition is actually a $(a_{1g},e_g) \rightarrow e_g$ transition in system due to the lower (D_{3d}) symmetry. [b] Room temperature, in 0.01 M KBH_4, ref 17. [c] Room temperature, in 0.1 M $NaClO_4$, ref 17.

to very substantial changes in the level scheme. The HOMO level $16a_2$ is still dominantly (92%) d_{xy}, and the LUMO $38a_1$ is 53% $d_{x^2-y^2}$, with the remaining contributions from ammonia; these d functions are of the wrong symmetry for mixing with dinitrogen. Mixing with π^* (roughly 13%) has lowered the $37a_1$, $15a_2$ (mostly d_{xz} and d_{yz}) by 0.3 eV; this mixing is quite important in interpretation of bridged binuclear complexes, since most models ignore bridge contributions to the occupied states (although Lauher has stressed[10] their importance). Our preliminary results on both the pyrazine-bridged and dinitrogen-bridged $[(NH_3)_5Ru]_2^V$ mixed-valence species indeed show such mixing.[25]

As indicated above, the predicted bonding and energy levels are very sensitive to distance. Table III gives the energies of states near the Fermi level as a function of Ru–N_2 distance. Both the σ and π interactions are expected to become stronger as the distance shortens, and, accordingly, both the total stabilization of the occupied d's and the total Ru positive charge increase with closer approach of the N_2 ligand.

B. Spectral Behavior. Koopmans' theorem is not valid in the Hartree–Fock–Slater scheme, and therefore we have calculated ionization potentials by using the transition state procedure.[19] For the hexaammines II and III, this yields predicted IP's of 16.04 and 23.36 eV; note that these are very much larger than the eigenvalues (orbital energies) discussed above. We also calculated the IP for III at the geometry of II and vice versa. These geometries differ[26] by 0.04 Å, and we calculate the IP's to differ by 0.04 eV.

The optical spectra are also calculated by a transition-state procedure. For the hexaammines, our results are presented in Table IV; the agreement with experiment[24,27] is very good, and the fairly small ϵ values are consistent with the formally forbidden nature of the transition. We also calculate the ligand → metal CT band ($7a_{2u} + 8e_u \rightarrow 10a_{1g}$) at 5.93 eV in III; thus this cannot be the low-lying optical band but might correspond to the stronger band ($\epsilon \simeq 475$) observed at 4.51 eV.[28]

In the more covalent species I, a strong band appearing[16] at 221 nm (5.61 eV; $\epsilon = 13\,000$) has been assigned to the Ru dπ → N π^* charge transfer; it should be strong due to good overlap and because, in the simplest two-site model, the transition is from a pair of π (*Ru* π + N π^*) to a pair of π^* (–Ru π + *N* $\tilde{\pi}^*$), a classic Mulliken[29] CT band. We find this transition ($37a_1 + 15a_2 \rightarrow 17a_2 + 40a_1$) at 5.1 eV for the Ru–N distance of 1.876 Å. (The excitation would be between e levels in C_{4v}, but these split due to the inequivalence of the H upon C_4 rotation). The ($16a_2 \rightarrow 17a_2 + 40a_1$), which is not forbidden but should be far weaker due to poorer overlap, occurs at 5.33 eV at this geometry. The relaxation effect is roughly 0.5 eV for these transitions; this substantial value arises from the considerable charge flow involved. The Mulliken charge on Ru goes up from 2.09 to 2.19, and the total on N_2 goes from –0.28 to –0.47 the excitation from $16a_2$. (In II and III there is less charge flow upon its d → d excitation, and the relaxation effect is only 0.1 eV.) The experimental optical band for I is broad enough to include both components.[30]

Comments

The good comparison of our calculated results with intuitive bonding concepts and with experimental optical spectra is encouraging for the use of DVM-HFS for other metal complexes, both organometallic and Werner-type. The use of flexible basis sets is necessary; the strong polarity in I, for instance, means that the basis functions on the four inequivalent types of N will differ considerably. The most striking feature of our calculations on the Allen–Senoff ion I are the extent of covalency and back-bonding and the considerable participation of the N π^* in the occupied orbitals $37a_1$ and $15a_2$. As noted above, this is of some interest in connection with intramolecular electron transfer, since it implies that localization in a mixed-valent species such as $[(NH_3)_5RuN]_2^{5+}$, even in a possible distorted (mixed-valence) geometry, may well still involve some density on the bridge. This would argue that such species might prefer[10,30] not to localize but to remain average valent (Robin/Day III). Work on this question is continuing.

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(31) **Note Added in Proof:** Since submission of this work an ab initio Hartree-Fock-Roothaan study of $(NH_3)_5RuN_2^{2+}$ has appeared [J. N. Murrell, A. Al-Derzi, G. J. Leigh, and M. F. Guest, *J. Chem. Soc. Dalton Trans.*, **8**, 1425 (1980)]. Their energy level diagrams and their predicted charge polarity agree well with ours; no excitation results are given.