

Electronic Structure of Transition-Metal Amide Ions $^+TiNH_2$, $^+VNH_2$, $^+CrNH_2$, and $^+MnNH_2$

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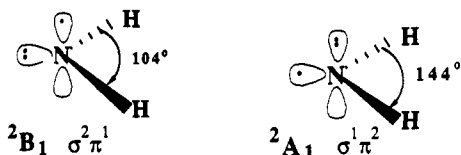
The electronic and geometric structures of the molecules $^+MNH_2$ ($M = Ti, V, Cr,$ and Mn) are reported and compared with available experimental data and previous theoretical studies on $^+ScNH_2$. The ground state of the systems studied results from the NH_2 group forming a double bond to the metal using its unpaired electron and the N lone pair. In addition to these low spin states there are low-lying high-spin states that are strongly (electrostatically) bound relative to the ground-state fragments. The energy gap between the high-spin and low-spin states decreases as one goes from left to right across the transition element series.

Introduction

Recently,¹ experimental bond energies for the transition-metal amide ions $^+ScNH_2$, $^+TiNH_2$, $^+VNH_2$, $^+CoNH_2$, $^+NiNH_2$, and $^+CuNH_2$ have been reported by Armentrout et al. These species are characterized by an M-N bond strength that is somewhat larger than anticipated and in particular is larger than that for the corresponding $^+M-CH_3$ species. This enhanced bond strength has been suggested¹ to arise from the dative interaction of the NH_2 lone pair with empty metal 3d orbitals and thus to be largest for the early transition-metal ions and to become substantially smaller for ions with no empty 3d orbitals. The role of the dative interaction was confirmed for the case of $^+ScNH_2$ by detailed ab initio calculations.^{2,3} In this report we extend our theoretical results on $^+MNH_2$ to include $M = Ti, V, Cr,$ and Mn . Our results confirm that the ground states of these systems result from the NH_2 group forming a double bond to the metal using its unpaired electron and the N lone pair.

Preliminaries

NH_2 has a 2B_1 ground state and a 2A_1 excited state approximately 32 kcal/mol higher.⁴

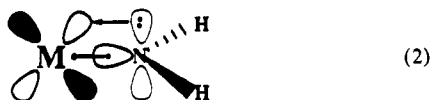


Our calculated energy separation is 34.8 kcal/mol. The geometry, total energies, and relative energies of these two states are recorded in Figure 1.

In the discussion of $^+ScNH_2$ we noted^{2,3} that these metal amide ions can be considered to arise from the ground 2B_1 state of NH_2 interacting with a dative bond in the σ system and a "covalent" π bond according to



Alternatively, we may consider the in situ NH_2 to be in the 2A_1 state and to interact with the metal via a dative bond in the π system and a "covalent" σ bond according to



Calling the first a $\sigma^2\pi$ interaction and the second a $\sigma\pi^2$ interaction, the equilibrium structure is

$$|^+MNH_2\rangle = C_1|\sigma^2\pi\rangle + C_2|\sigma\pi^2\rangle$$

Note that in this representation only one metal electron is used in the bonding. Consequently, when the metal is doubly bonded to the amide group



the number of unpaired or spectator electrons on M is 2 for Ti, 3 for V, 4 for Cr, and 5 for Mn. For Ti, for example, the two spectator electrons can be allotted to the various 3d orbitals in 10 different ways (triplet coupled), and we expect the relative energies of these triplets to depend on the extent to which they interfere with the bonding picture given above. If, for example, one of the spectator electrons is a $3d\sigma$, we expect both $\sigma^2\pi$ and $\sigma\pi^2$ interactions to be diminished. The $\sigma^2\pi$ interaction corresponding to eq 1 is compromised because the $3d\sigma$ space on the metal is occupied and the dative interaction is restricted to the metal 4s and 4p σ . A $3d\sigma$ spectator electron compromises the $\sigma\pi^2$ interaction by forcing the double occupancy of the metal σ space. The Lewis structures would be



In a similar way a $3d\pi_x$ spectator electron would "turn off" the π -bonding component of the $\sigma^2\pi$ interaction shown in eq 1 and would diminish the π -bonding component of eq 2. The resulting Lewis structures would be



It is quite likely that the geometry (planarity/nonplanarity) would be affected. Putting a spectator electron in both the $3d\sigma$ and $3d\pi_x$ orbitals would of course have the largest effect.

We recognize that these structures represent the extremes in the bonding picture and the inevitable orbital polarization and

(1) (a) Clemmer, D. E.; Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* 1990, 94, 3008-3015. (b) Clemmer, D. E.; Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* 1990, 94, 208-217. (c) Clemmer, D. E.; Armentrout, P. B. *J. Phys. Chem.* 1991, 95, 3084.

(2) Mavridis, A.; Kunze, K.; Harrison, J. F.; Allison, J. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990; Chapter 18.

(3) Mavridis, A.; Herrera, F. L.; Harrison, J. F. The Electronic and Geometric Structure of $^+ScNH_2$ and $^+ScNH_3$. *J. Phys. Chem.*, preceding paper in this issue.

(4) Johns, J. W. C.; Ramsey, D. A.; Ross, S. C. *Can. J. Phys.* 1976, 54, 1804.

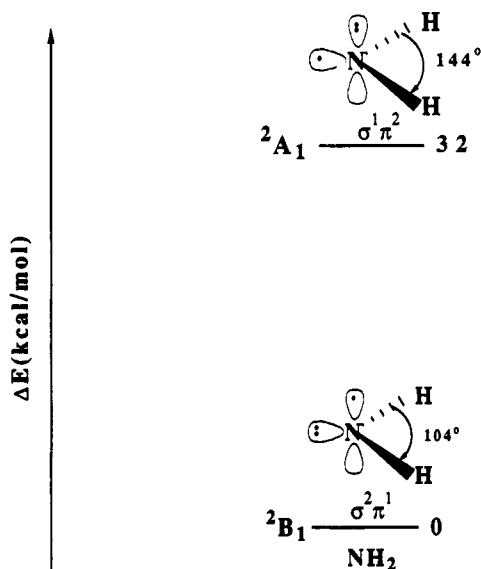
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TABLE I: Energies E (au), Metal–Nitrogen Bond Distances $R_{\text{Ti-N}}$ (Å), Dissociation Energies D_0 (kcal mol⁻¹) for Seven Low-Lying States of the TiNH_2^+ , and System Net Charges Q As Obtained from Mulliken Population Analysis at the GVB(4/8) Level of Computation

state	method	E , au	$R_{\text{Ti-N}}$, Å	D_0^a , kcal mol ⁻¹	Q (Ti, N, 2H)
3B_2 ($d\delta_+$, $d\pi_y$)	SCF	-903.838 76	1.942	42.6	
	GVB(4/8)	-903.888 24	1.956	53.6	+1.34, -0.69, +0.35
	GVB+1+2	-904.055 93	1.949	69.2	
3B_1 ($d\delta_-$, $d\pi_y$)	SCF	-903.835 77	1.916	40.7	
	GVB(4/8)	-903.884 51	1.936	51.2	+1.33, -0.70, +0.36
	GVB+1+2	-904.052 52	1.943	67.1	
3A_2 ($d\sigma$, $d\delta_-$)	SCF	-903.824 93	1.941	33.9	
	GVB(4/8)	-903.874 83	1.938	45.1	+1.32, -0.71, +0.39
	GVB+1+2	-904.045 30	1.928	62.5	
3A_1 ($d\sigma$, $d\delta_+$)	SCF	-903.823 96	1.945	33.3	
	GVB(4/8)	-903.873 72	1.943	44.6	+1.32, -0.72, +0.39
	GVB+1+2	-904.044 23	1.931	61.9	
3B_1 ($d\delta_+$, $d\pi_x$)	SCF	-903.821 23	1.987	31.6	
	GVB(4/8)	-903.866 10	1.989	39.7	+1.42, -0.78, +0.37
	GVB+1+2	-903.031 53	1.995	53.9	
3B_2 ($d\delta_-$, $d\pi_x$)	SCF	-903.814 85	1.982	27.6	
	GVB(4/8)	-903.859 79	1.984	35.7	+1.42, -0.78, +0.36
	GVB+1+2	-904.025 28	1.989	50.0	
3A_2 ($d\pi_y$, $d\pi_x$)	SCF	-903.802 07	1.992	19.6	
	GVB(4/8)	-903.847 52	1.995	28.0	+1.39, -0.74, +0.35
	GVB+1+2	-904.011 77	2.006	41.5	

^aAll D_0 have been calculated with respect to the free products: in their ground state, $D_0(\text{SCF})$ with respect to $\text{Ti}^+(\text{F,SCF}) + \text{NH}_2(^2B_1, \text{SCF})$, $D_0(\text{GVB}(4/8))$ with respect to $\text{Ti}^+(\text{F,SCF}) + (\text{NH}_2(^2B_1, \text{GVB}(3/6)))$, and $D_0(\text{GVB}+1+2)$ with respect to $\text{Ti}^+(\text{F,SCF}) + \text{NH}_2(^2B_1, \text{GVB}(3/6)+1+2)$. Therefore, the binding energies reported above can be considered as lower limits.


Figure 1. Relative energies of the low-lying states of NH_2 .

charge transfer will blur the distinctions. Nonetheless, we believe the electronic structure of these molecules can be profitably viewed from this perspective. These effects are summarized in Figure 2.

The preceding discussion assumes that one component of the chemical bond between the metal and NH_2 (either σ or π) results from the singlet coupling of an electron on M with one on NH_2 .

As noted, previously,^{5,6} the energy required to uncouple a metal d electron to allow its participation in a bond increases with the number of d electrons on the metal (exchange energy loss).^{5,6} All things being equal, this effect will dictate that the $^+\text{M-NH}_2$ bond strength decrease in going from Sc^+ to Cr^+ as found in our calculations.

In addition to this low-spin coupling, one may generate a high-spin molecule by keeping the number of unpaired electrons in the molecule equal to the number in the separated fragments.

Since a chemical bond may still arise because of the dative interactions shown in eqs 1 and 2, we may consider the high-spin molecule as having only one bond (σ or π). However, because the metal is positively charged, its electrostatic interaction with the dipole moment (permanent or induced) of the NH_2 will contribute to the molecules stability, regardless of the spin of the system.

We may distinguish between dative and electrostatic interactions by monitoring the number of electrons transferred from the NH_2 σ or π system to the metal. Our results show that there is very little charge transfer in the high-spin states and suggest strongly that the interaction is dominated by electrostatics. Supporting this interpretation is the insensitivity of the calculated metal- NH_2 bond energies in the high-spin systems to the metal, ranging between 29 and 34 kcal/mol.

Both low-spin and high-spin bonding modes will be discussed and illustrated for various states of $^+\text{TiNH}_2$, $^+\text{VNH}_2$, $^+\text{CrNH}_2$, and $^+\text{MnNH}_2$.

Computational Details

The basis sets used, computational techniques, and electronic structure codes have been described previously.^{3,7} We will focus here on those aspects of the computation that are specific to the $^+\text{MNH}_2$ systems.

Low-Spin States. The $^+\text{TiNH}_2$ molecule was restricted to being planar and to having C_{2v} symmetry. Self-consistent field (SCF) solutions were obtained for seven of the ten possible states formed by allotting the two spectator electrons among the five 3d orbitals. SCF calculations on the three missing states, 3B_1 ($d\sigma$, $d\pi_x$), 3B_2 ($d\sigma$, $d\pi_y$), and 3A_2 ($d\delta_+$, $d\delta_-$), collapsed to the lower states of the same symmetry, 3B_1 ($d\delta_+$, $d\pi_x$), 3B_2 ($d\delta_+$, $d\pi_y$), and 3A_2 ($d\sigma$, $d\delta_-$) respectively. Generalized valence bond⁸ (GVB(4/8)) and configuration interaction (GVB(4/8)+1+2) calculations were performed on these seven states in C_{2v} symmetry using basis sets described previously. The results are collected in Tables I and II and Figure 3. The notation GVB(4/8) implies that the four bonds in the molecule (metal-nitrogen σ and π and two N-H σ bonds) are correlated in a perfect pairing sense, resulting in a 16

(5) Carter, E. A.; Goddard, W. A., III. *J. Phys. Chem.* 1984, 88, 1485.

(6) Alvarado-Swaigood, A.; Harrison, J. F. *THEOCHEM* 1988, 169, 155.

(7) Kunze, K.; Harrison, J. F. *J. Am. Chem. Soc.* 1990, 112, 3812.

(8) Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* 1973, 6, 368.

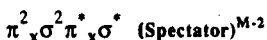
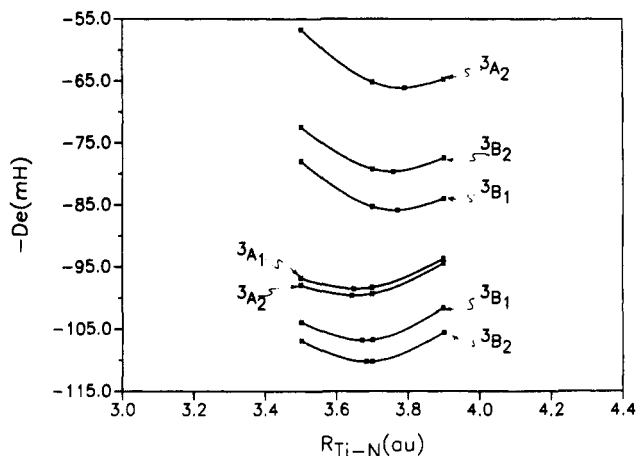
TABLE II: Mulliken Equilibrium Population Analysis for TiNH_2^+ for Seven Different States As Obtained from GVB(4/8) Calculations

state	Ti^+									N				totals		
	3d σ	3d δ_+	3d π_x	3d π_y	3d δ_-	4s	4p $_x$	4p $_y$	4p $_z$	2p $_x$	2p $_y$	2p $_z$	2s	Π_x	Ti	N
3B_2 (3d δ , 3d π_y)	0.21	0.94	0.27	1.00	0.00	0.10	0.10	0.00	0.03	1.59	1.19	1.37	1.52	1.96	2.62	5.67
3B_1 (3d δ_- , 3d π_y)	0.16	0.01	0.28	1.00	1.00	0.10	0.09	0.01	0.03	1.58	1.19	1.38	1.52	1.95	2.68	5.67
3A_2 (3d σ , 3d δ_-)	0.88	0.08	0.30	0.01	1.00	0.28	0.09	0.00	0.05	1.56	1.20	1.39	1.53	1.95	2.69	5.68
3A_1 (3d δ_+ , 3d σ)	0.95	1.00	0.29	0.02	0.00	0.29	0.09	0.00	0.05	1.58	1.20	1.39	1.54	1.96	2.69	5.71
3B_1 (3d δ_+ , 3d π_x)	0.26	0.91	1.08	0.02	0.00	0.13	0.15	0.01	0.04	1.71	1.19	1.35	1.51	2.94	2.60	5.76
3B_2 (3d δ_- , 3d π_x)	0.19	0.00	1.08	0.02	1.00	0.11	0.15	0.01	0.03	1.72	1.19	1.35	1.51	2.95	2.59	5.77
3A_2 (3d π_x , 3d π_y)	0.17	0.00	1.09	1.00	0.00	0.12	0.17	0.01	0.04	1.69	1.18	1.34	1.51	2.95	2.60	5.72

Electron Configuration

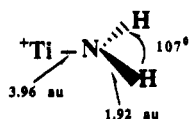
Contributing Structures

Comments

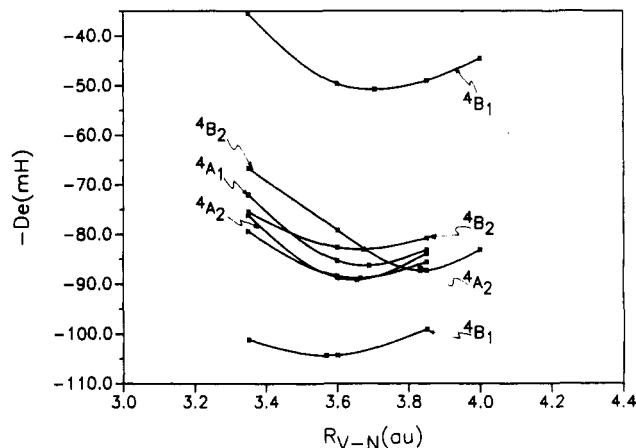
Spectator electrons not dx or d σ .Spectator electron of σ symmetry. Both structures will continue to contribute because of interplay between 3d σ and 4s.Spectator electron of π_x symmetry. This will force structure with 3 π_x electrons and singlet coupled pair on N.Spectator electrons of both π_x and σ symmetry. No π bond and weakened σ bond.Figure 2. Various Lewis structures for the low-lying electronic states of MNH_2^+ .Figure 3. Potential energy curves around equilibrium of the $^+\text{TiNH}_2$ system for seven states at the GVB(4/8)+1+2 level. Numbers on the ordinate give binding energies with respect to ground-state products.

configuration state function (CSF) wave function. The notation GVB(4/8)+1+2 means that all single and double excitations were included from the eight bonding electrons in each of these 16 configurations. The two spectator electrons were kept at the SCF level.

The geometry of $^+\text{TiNH}_2$ in the 3B_2 ($d\delta_+$, $d\pi_y$) state was optimized at the GVB(4/8) level. The resulting C_{2v} geometry is



If one removes the C_{2v} constraint the resulting GVB(4/8) geometry is pyramidal with the Ti $\sim 15^\circ$ out of the NH_2 plane and the molecular energy ~ 1.3 kcal/mol lower than the planar symmetry. It is quite likely that all of the states of $^+\text{TiNH}_2$ which we will discuss are nonplanar and the A_1 and B_1 symmetries will mix and become A' while the A_2 and B_2 will become A'' . Because

Figure 4. Potential energy curves around equilibrium of the $^+\text{VNH}_2$ system for seven states at the GVB(4/8)+1+2 level. Numbers on the ordinate give binding energies with respect to ground-state products.

of the anticipated small energy difference between the planar and nonplanar structures we will restrict our attention to the planar structures for all metals discussed in this paper.

In addition to the planar restriction, the NH bond length and the NH_2 bond angles were fixed at the computed 3B_2 (GVB(4/8)) values for the seven states of $^+\text{TiNH}_2$.

The procedure for $^+\text{VNH}_2$, $^+\text{CrNH}_2$, and $^+\text{MnNH}_2$ was similar. The V^+ cation has a $3d^4$ configuration⁹ which gives rise to a 5D ground state with a 3F ($3d^4s^1$) state 0.336 eV higher. At the SCF level these two states are inverted, the 3F being the ground state with the 5D 0.251 eV higher. At the SCF+1+2 level the experimental order is restored with the 3F state 0.126 eV above the 5D . If we singlet couple one of the four valence electrons on V^+ with the unpaired electron on NH_2 , we have three spectator electrons remaining on V^+ . Singly occupying each 3d orbital results in 10 quartet states of C_{2v} symmetry. SCF calculations

(9) Moore, C. E. *Atomic Energy Levels*; NSRDS-NBS 35; National Bureau of Standards: Washington, DC, 1971.

TABLE III: Energies E (au), Vanadium–Nitrogen Bond Distances V–N (Å), Dissociation Energies D_e (kcal mol⁻¹) for Seven Low-Lying States of the VN₂⁺ System, and Net Charges Q As Obtained from Mulliken Population Analysis at the GVB(4/8) Level of Computation

state	method	E/E_H	R_{V-N} , Å	D_e^a , kcal mol ⁻¹	Q (V, N, 2H)
⁴ B ₁ (dδ ₊ , dπ _y , dδ ₋)	SCF	-998.299 43	1.885	37.2	
	GVB(4/8)	-998.348 61	1.906	47.8	+1.32, -0.70, +0.38
	GVB+1+2	-998.480 83	1.888	65.5	
⁴ A ₂ (dδ ₊ , dπ _y , dπ _x)	SCF	-998.289 60	1.922	31.1	
	GVB(4/8)	-998.335 01	1.945	39.3	+1.38, -0.75, +0.36
	GVB+1+2	-998.465 60	1.934	56.0	
⁴ A ₂ (dσ, dδ ₊ , dδ ₋)	SCF	-998.283 06	1.908	27.0	
	GVB(4/8)	-998.332 90	1.928	38.0	+1.32, -0.72, +0.40
	GVB+1+2	-998.465 26	1.939	55.7	
⁴ B ₂ (dδ ₊ , dπ _x , dδ ₋)	SCF	-998.881 85	1.929	26.2	
	GVB(4/8)	-998.326 72	1.952	34.1	+1.40, -0.78, +0.38
	GVB+1+2	-998.463 79	2.028	54.8	
⁴ A ₁ (dπ _y , dπ _x , dδ ₋)	SCF	-998.289 53	1.923	31.0	
	GVB(4/8)	-998.334 95	1.945	39.3	+1.38, -0.75, +0.36
	GVB+1+2	-998.462 75	1.952	54.2	
⁴ B ₂ (dσ, dδ ₊ , dπ _y)	SCF	-998.275 94	1.898	22.5	
	GVB(4/8)	-998.327 34	1.916	34.5	+1.27, -0.66, +0.39
	GVB+1+2	-998.459 47	1.944	52.1	
⁴ B ₁ (dσ, dδ ₊ , dπ _x)	SCF	-998.254 40	1.955	9.0	
	GVB(4/8)	-998.299 49	1.972	17.0	+1.35, -0.73, +0.38
	GVB+1+2	-998.427 25	1.961	31.9	

^aSee footnote a, Table I.

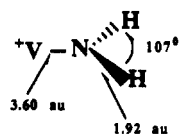
TABLE IV: Mulliken Equilibrium Population Analysis for VN₂⁺ for Seven Different States As Obtained from GVB(4/8) Calculations

state	V ⁺									N				totals		
	3dσ	3dδ ₊	3dπ _x	3dπ _y	3dδ ₋	4s	4p _x	4p _y	4p _z	2s	2p _x	2p _y	2p _z	Π _x	Ti	N
⁴ B ₁ (3dδ ₊ , 3dπ _y , 3dδ ₋)	0.44	0.69	0.28	1.00	1.00	0.14	0.09	0.01	0.04	1.52	1.58	1.20	1.37	1.95	3.69	5.67
⁴ A ₂ (3dδ ₊ , 3dπ _x , 3dπ _y)	0.19	1.00	1.10	1.00	0.00	0.13	0.15	0.01	0.04	1.51	1.70	1.19	1.33	2.95	3.62	5.73
⁴ A ₁ (3dπ _x , 3dπ _y , 3dδ ₋)	0.19	0.00	1.09	1.00	1.00	0.13	0.15	0.01	0.04	1.51	1.70	1.19	1.33	2.94	3.61	5.73
⁴ A ₂ (3dσ, 3dδ ₊ , 3dδ ₋)	1.01	1.00	0.31	0.02	1.00	0.21	0.09	0.00	0.06	1.53	1.55	1.21	1.40	1.95	3.70	5.69
⁴ B ₂ (3dδ ₊ , 3dπ _x , 3dδ ₋)	0.48	0.65	1.10	0.03	1.00	0.17	0.14	0.01	0.05	1.51	1.71	1.20	1.35	2.95	3.63	5.75
⁴ B ₂ (3dσ, 3dδ ₊ , 3dπ _y)	0.98	1.00	0.34	1.00	0.00	0.26	0.10	0.01	0.06	1.53	1.52	1.20	1.39	1.96	3.75	5.64
⁴ B ₁ (3dσ, 3dδ ₊ , 3dπ _x)	1.01	1.00	1.09	0.02	0.00	0.30	0.15	0.01	0.09	1.50	1.71	1.19	1.31	2.95	3.67	5.71

TABLE V: Energies E (au), Metal–Nitrogen Bond Distances Cr–N (Å), Dissociation Energies D_e (kcal mol⁻¹), and Net Charges As Obtained from Mulliken Population Analysis at the GVB(2/4) and GVB(4/8) Level for CrNH₂⁺

state	method	E/E_H	R_{Cr-N} , Å	D_e , kcal mol ⁻¹	Q (Cr, N, 2H)
³ B ₁ (3dσ, 3dδ ₊ , 3dπ _y , 3dδ ₋)	SCF	-1098.707 13	1.870	7.8	
	GVB(2/4)	-1098.739 97	1.890	17.1	+1.26, -0.66, +0.41
	GVB(4/8)	-1098.759 49	1.890	20.4	+1.25, -0.65, +0.40
	GVB(2/4)+1+2	-1098.847 24	1.888	40.1	
³ A ₁ (3dδ ₊ , 3dπ _x , 3dπ _y , 3dδ ₋)	SCF	-1098.712 50	1.873	11.2	
	GVB(2/4)	-1098.739 47	1.896	16.8	+1.37, -0.75, +0.38
	GVB(4/8)	-1098.758 34	1.896	19.7	+1.37, -0.75, +0.37
	GVB(2/4)+1+2	-1098.830 00	1.872	29.3	
³ B ₂ (3dσ, 3dδ ₊ , 3dπ _x , 3dδ ₋)	SCF	-1098.684 81	1.924	-6.2	
	GVB(1/2)	-1098.710 49	1.954	-1.4	+1.34, -0.74, +0.40
	GVB(4/8)	-1098.729 46	1.953	1.6	+1.34, -0.73, +0.38
	GVB(2/4)+1+2	-1098.797 93	1.912	9.2	
³ A ₂ (3dσ, 3dδ ₊ , 3dπ _y , 3dπ _x)	SCF	-1098.676 84	1.921	-11.2	
	GVB(1/2)	-1098.703 64	1.952	-5.7	+1.31, -0.70, +0.39
	GVB(4/8)	-1098.722 60	1.951	-2.7	+1.31, -0.69, +0.38
	GVB(2/4)+1+2	-1098.792 53	1.910	5.6	

on the three states ⁴A₂ (3dσ, 3dπ_x, 3dπ_y), ⁴B₂ (3dσ, 3dπ_x, 3dδ₋), and ⁴B₁ (3dσ, 3dπ_y, 3dδ₋) collapsed to the lower states of the same symmetry, ⁴A₂ (3dδ₊, 3dπ_x, 3dπ_y), ⁴B₂ (3dδ₊, 3dπ_x, 3dδ₋), and ⁴B₁ (3dδ₊, 3dπ_y, 3dδ₋), respectively. SCF, GVB(4/8), and configuration interaction calculation were carried out on the remaining seven states in C_{2v} symmetry. The results are collected in Tables III and IV and Figure 4. The ground state is the ⁴B₁ (3dδ₊, 3dπ_y, 3dδ₋), and it has the optimal GVB(4/8) geometry



The geometry of the NH₂ group is exactly that found in ⁺TiNH₂, and this NH bond length and NH₂ angle were used for all subsequent calculations on ⁺VNH₂. The dissociation energies have been computed with respect to the ground-state fragments as described for ⁺TiNH₂.

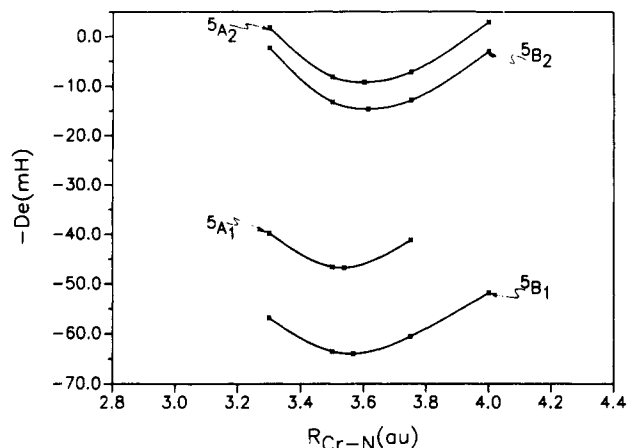
The Cr⁺ cation has an electronic d⁵ configuration⁹ which gives rise to a spherical ⁶S ground state. The first excited state is of ⁶D symmetry, is 1.522 eV above the ⁶S, and results from the 3d⁴4s¹ configuration. Singlet coupling a 3d on Cr to an unpaired electron on NH₂ leaves four high-spin spectator electrons on Cr. Singly occupying each of the 3d orbitals results in five states of C_{2v} symmetry. SCF and GVB calculation on the ³A₁ (3dσ, 3dπ_x, 3dπ_y, 3dδ₋) collapsed to the ³A₁ (3dδ₊, 3dπ_x, 3dπ_y, 3dδ₋) state. SCF, GVB(2/4), GVB(4/8), and GVB(2/4)+1+2 calculations were

TABLE VI: Mulliken Equilibrium Population Analysis for Selected Orbitals in CrNH₂⁺ for Four Different States As Obtained from GVB(4/8) Calculations

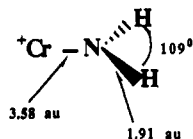
state	Cr ⁺										N				totals		
	3dσ	3dδ ₊	3dπ _x	3dπ _y	3dδ ₋	4s	4p _x	4p _y	4p _z	2s	2p _x	2p _y	2p _z	Π _x	Cr	N	
⁵ B ₁ (3dσ, 3dδ ₊ , 3dπ _y , 3dδ ₋)	1.01	1.00	0.38	1.00	1.00	0.21	0.10	0.01	0.01	1.53	1.49	1.21	1.40	1.97	4.72	5.63	
⁵ A ₁ (3dδ ₊ , 3dπ _y , 3dπ _x , 3dδ ₋)	0.22	1.00	1.09	1.01	1.00	0.13	0.14	0.01	0.04	1.50	1.71	1.19	1.32	2.94	4.64	5.72	
⁵ B ₂ (3dσ, 3dδ ₊ , 3dπ _x , 3dδ ₋)	1.03	1.00	1.09	0.02	1.00	0.29	0.14	0.01	0.09	1.49	1.71	1.19	1.32	2.94	4.67	5.71	
⁵ A ₂ (3dσ, 3dδ ₊ , 3dπ _x , 3dπ _y)	1.02	1.00	1.10	1.01	0.00	0.32	0.16	0.02	0.09	1.49	1.69	1.19	1.30	2.95	4.72	5.67	

TABLE VII: Energies (au), Mn-N Bond Distances (Å), Dissociation Energies D_e (kcal mol⁻¹), and Net Charges As Obtained for Mulliken Population Analysis of the ⁶A₁ Ground State of MnNH₂⁺

state	method	E, au	R _{M-N} , Å	D _e , kcal mol ⁻¹	Q (Mn, N, 2H)
⁶ A ₁	GVB(2/4)	-1205.24993	1.926	18.6	+1.32, -0.72, +0.40
	GVB(4/8)	-1205.26893	1.925	21.6	+1.32, -0.70, +0.38
	GVB(2/4)+1+2	-1205.34759	1.889	42.6	

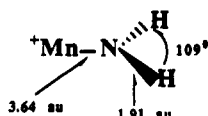
**Figure 5.** Potential energy curves around equilibrium of the ⁺CrNH₂ system for four states at the GVB(2/4)+1+2 level. Numbers on the ordinate give binding energies with respect to ground-state products.

carried out on states of ⁵A₁, ⁵A₂, ⁵B₁, and ⁵B₂ symmetries, and the results are collected in Tables V and VI and Figure 5. The GVB(2/4) notation implies that only the two electron pairs involved in the metal-nitrogen bonding are correlated in a perfect pairing sense. The resulting GVB(2/4)+1+2 calculations maintain the NH bonds at the SCF level. The geometry of the ground ⁵A₁ state was optimized at the GVB(4/8) level.



These NH₂ parameters were used in all ⁺CrNH₂ calculations.

The Mn⁺ cation has an electronic configuration ⁹3d⁵4s¹ which gives rise to a ⁷S ground state. The first excited state is of ⁵S symmetry and also results from the 3d⁵4s configuration. Singlet coupling the 4s electron to an unpaired electron on NH₂ leaves five high-spin spectator electrons on Mn⁺. Consequently, we have only the ⁶A₁ state to consider. The geometry of this state was fully optimized at the GVB(4/8) level, and the resulting NH₂ geometry was used in all higher level calculations. The GVB(4/8) geometry is



In addition to the GVB(4/8) calculation we carried out GVB(2/4) and GVB(2/4)+1+2 calculations as described for ⁺CrNH₂. The results are summarized in Table VII.

TABLE VIII: Bond Distances R_{M-N}, Binding Energies D_e, and Net Charges on the Metal for MNH₂⁺ Ground States from Sc⁺ to Mn⁺

system, state, method	R _{M-N} , Å	D _e , kcal mol ⁻¹	D ₀ ^{exptl} , kcal mol ⁻¹	net Q on M [from GVB(4/8) functions]
ScNH ₂ ⁺ , ² A ₂ , MCSCF(2/4)+1+2	1.981	79.0	85 ± 2	+1.41 ^a
TiNH ₂ ⁺ , ³ B ₂ , GVB(4/8)+1+2	1.949	69.2	85 ± 3	+1.34
VNH ₂ ⁺ , ⁴ B ₁ , GVB(4/8)+1+2	1.888	65.5	73 ± 2	+1.32
CrNH ₂ ⁺ , ⁵ B ₁ , GVB(2/4)+1+2	1.888	40.1		+1.24
MnNH ₂ ⁺ , ⁶ A ₁ , GVB(2/4)+1+2	1.889	42.6		+1.32

^a From GVB(4/8) calculations.

TABLE IX: Comparison of ⁺MCH₃, ⁺MCH₂, and ⁺MNH₂ Bond Lengths (Å)

	CH ₃	CH ₂	NH ₂
Sc ⁺	2.25	2.00	1.98
Ti ⁺	2.20	1.97	1.95
V ⁺	2.17	1.96	1.89
Cr ⁺	2.14	1.92	1.89

The Mulliken population for this state predicts a charge distribution similar to the metal amides discussed earlier. In particular the total number of electrons in the π_x system is 2.95, the total in the metal valence orbitals is 5.70, and the total in the N valence shell is 5.70.

High-Spin States. The high-spin states were all computed at the SCF level. In C_{2v} symmetry the ground states correspond to the ground electronic state of M⁺ interacting with the ²B₁ state of NH₂. For Ti⁺ we selected the 4s3dπ_x3dπ_y configuration; for V⁺, 4s3d³, with the 3dσ and 3dδ₊ being empty; for Cr⁺, 3d⁵; and for Mn⁺, the 4s3d⁵ configuration. SCF calculations were done for ⁺TiNH₂ (⁵B₂), ⁺VNH₂ (⁶A₁), ⁺CrNH₂ (⁷B₁), and ⁺MnNH₂ (⁸B₁). The energies, geometries, and electron distribution are collected in Table VIII.

Results

Low-Spin States. Tables I-VII contain details of the energies, geometries, and electron distributions for the low-spin states of the four molecules ⁺TiNH₂, ⁺VNH₂, ⁺CrNH₂, and ⁺MnNH₂. Figures 3-5 show the energy versus M-N distance for these electronic states. Several observations are noteworthy:

(a) The calculated bond energies decrease along the series ⁺TiNH₂ (69 kcal/mol) > ⁺VNH₂ (66 kcal/mol) > ⁺CrNH₂ (40 kcal/mol), ⁺MnNH₂ (43 kcal/mol) being similar to ⁺CrNH₂. This is in qualitative agreement with expectations^{5,6} based on exchange energy loss.

(b) The electronic configuration of the ground state has the minimum number of 3dσ and 3dπ_x spectator electrons possible. This is zero for ⁺TiNH₂, one for ⁺VNH₂ and ⁺CrNH₂, and two for ⁺MnNH₂.

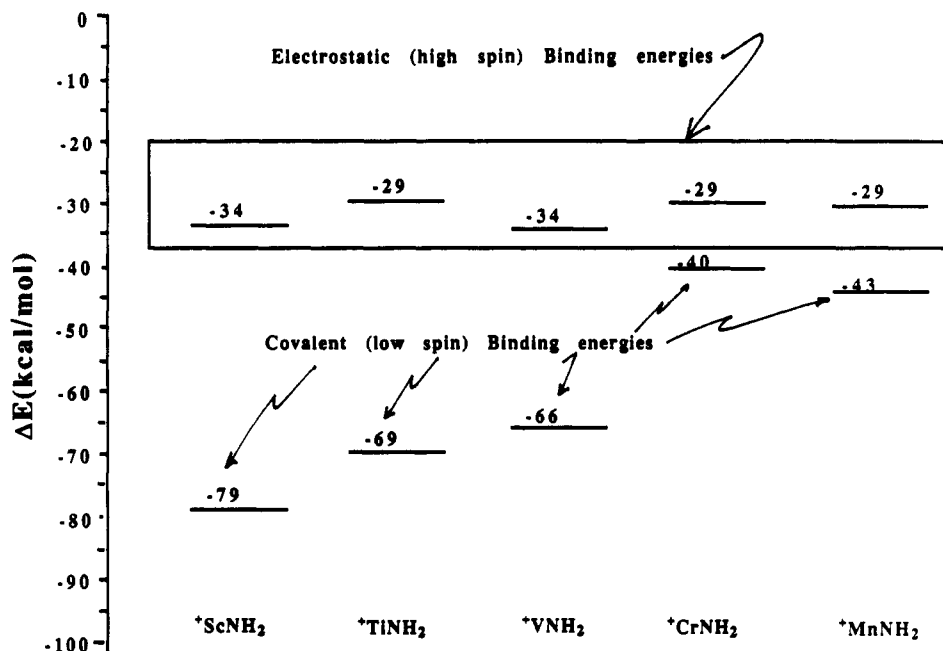


Figure 6. Binding energies of lowest low-spin and lowest high-spin states of $^+MNH_2$.

TABLE X: Dissociation Energy, Metal-Nitrogen Bond Length, and Charge on Metal in Various High-Spin States of $^+MNH_2$

system (state)	R_{M-N} , Å	D_e , kcal mol $^{-1}$	net Q on M
$^+ScNH_2$ (4B_2)	2.38	34	
$^+TiNH_2$ (3B_2)	2.38	29	+0.90
$^+VNH_2$ (6A_1)	2.28	34	+0.89
$^+CrNH_2$ (7B_1)	2.32	29	+0.91
$^+MnNH_2$ (8B_1)	2.39	29	+0.88

(c) The electronic configuration of the highest lying state of $^+MNH_2$ has both a $3d\sigma$ and $3d\pi_x$ spectator electron.

(d) The bond energies are much more sensitive to the metal than the M-N bond lengths. Our calculated bond lengths are as follows: $^+TiNH_2$ (1.95 Å), $^+VNH_2$ (1.89 Å), $^+CrNH_2$ (1.89 Å), and $^+MnNH_2$ (1.89 Å).

(e) In Table IX we compare the calculated bond lengths⁶ for $^+MCH_2$, $^+MCH_2$, and $^+MNH_2$. The amide bond lengths are more similar to the methylene bond lengths than to the methyl bond lengths, consistent with our interpretation that NH_2 is doubly bonded to the metal.

(f) In all states and for all molecules the metal loses electrons to the NH_2 group: the charges on the metals in the molecular ground state are Ti (+1.34), V (+1.32), Cr (+1.26), and Mn (+1.32).

These results are summarized and compared with experiment in Table X. For completeness, we have included theoretical results published^{2,3} earlier for $^+ScNH_2$. In each case where there is an experimental value our calculated result is low. The errors are 7%, 19%, and 11% for $^+ScNH_2$, $^+TiNH_2$, and $^+VNH_2$, respectively.

High-Spin States. From Table VIII we see that the high-spin states are all bound at the SCF level and all have comparable

M-N bond energies and bond lengths: $^+TiNH_2$ (3B_2 ; 29 kcal/mol, 2.38 Å), $^+VNH_2$ (6A_1 ; 34 kcal/mol, 2.28 Å), $^+CrNH_2$ (7B_1 ; 29 kcal/mol, 2.38 Å), and $^+MnNH_2$ (8B_1 ; 29 kcal/mol, 2.38 Å).

The relatively small charge transfer coupled with the uniformity of bond energies and bond lengths argues persuasively that the metal- NH_2 interaction is primarily electrostatic.¹⁰ Note that because the "covalent" bond energies tend to decrease as the number of d electrons on the metal increase and the electrostatic energies remain approximately constant, the energy gap between the high-spin, electrostatic states and the low-spin covalent states decreases as we go from left to right in the transition series. This is illustrated in Figure 6 ($^+ScNH_2$ data from ref 3).

Conclusions

While several detailed conclusions have been drawn, there are two of general significance. First, the NH_2 group forms a double bond to the transition-metal ions and is therefore more like a metal-carbene than a metal-methyl. Second, there are low-lying, high-spin states of these molecules which become competitive for the ground state as one moves from left to right across the transition element series.

Acknowledgment. This work was partially supported under NSF Grant CHE8519752 (J.F.H.), as well as NATO Grant GRE890502 to A.M. and J.F.H. The electronic structure codes provided by the Argonne theory group have been indispensable to this work.

(10) For other examples of electrostatic effects in transition-metal bonding see: Rivera, M.; Harrison, J. F.; Alvarado-Swaisgood, A. *J. Phys. Chem.* 1990, 94, 6969 and references therein.