den by the much more intense charge-transfer bands. Of the two low-lying weak bands that do occur in the electronic spectrum of Co(sacsac)$_2$, the band at 10,870 cm^{-1} correlates nicely with the prediction from calculations based on epr data that $d_{xz} \rightarrow d_{z^2}$ ($^2A_g \rightarrow {}^2B_{2g}$) should be seen around 10,000 cm^{-1}. The band at 6750 cm^{-1} may be associated with the $d_{x^2-y^2} \rightarrow d_{z^2}$ ($^2A_g \rightarrow {}^2A_g$) transition, and the low-energy $d_{yz} \rightarrow d_{z^2}$ ($^2A_g \rightarrow {}^2B_{3g}$) transition, predicted by epr results to be $\sim$1900 cm^{-1}, would appear in the infrared region.

The model for effects of axial ligation, originally proposed for Cu(II) chelate complexes,[8] predicts that the principal effects of axial ligation are (1) the d_{xy} is lowered in energy by the metal moving slightly out of the plane of chelate donor atoms, (2) the d_{z^2} is elevated because of interaction with the ligand coordinated along the z axis, and (3) movement of the metal out of the plane destabilizes d_{xz} but has little effect on d_{yz} or $d_{x^2-y^2}$.

The proposed d energy level ordering for Co(sacsac)$_2$ and the 1:1 adduct with piperidine are presented in Figure 2. All experimental observations are consistent with the model. The decrease in d_{xz}–d_{yz} separation determined from the epr parameters is expected from this model. The calculated d_{xz}–d_{z^2} separation remains almost constant which is also compatible, since both levels are destabilized upon adduct formation. The energy of the d_{yz} level is relatively unchanged and so the d_{yz}–d_{z^2} separation increases.

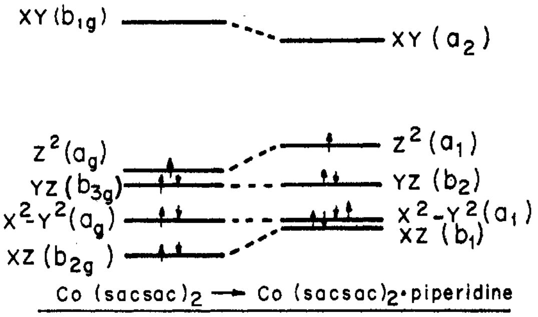

Figure 2.—Proposed d energy level orderings for Co(sacsac)$_2$ and Co(sacsac)$_2$·pip.

The observed effects of axial ligation on the electronic structure of this low-spin Co(II) complex is thus compatible with the model applied to adducts of Cu(II) chelates. These observations encourage further studies to examine the general structural and electronic effects associated with adduct formation of planar transition metal complexes.

Experimental Section

Co(sacsac)$_2$ was prepared according to a previously reported method.[5,13] Elemental analyses for C, H, and S were performed by Galbraith Laboratories, Knoxville, Tenn. *Anal.* Calcd for Co(sacsac)$_2$: C, 37.37; H, 4.40; S, 39.90. Found: C, 37.53; H, 4.45; S, 40.12. The crystalline solid was stored in a desiccator or under vacuum.

Samples were prepared for epr studies on a vacuum line by distilling amine and solvent into quartz tubes containing degassed, solid Co(sacsac)$_2$. Samples were thoroughly degassed and sealed to prevent contact with air. (The solutions are very air sensitive, changing in a matter of seconds from deep green to amber upon contact with air. The adducts in solution must be scrupulously protected from atmospheric contact.) Spectra were collected on a Varian X-band spectrometer. Samples were used as frozen solutions at 130°K, with temperature controlled by a Varian variable-temperature control unit.

Electronic spectra were collected on a Cary 14 spectrophotometer. Samples were prepared from rigorously degassed materials in an inert-atmosphere box filled with an argon–hydrogen mixture and sealed in Infracil cells.

Acknowledgment.—The authors wish to acknowledge the support of the research by the Advanced Research Projects Agency through Contract No. DAHC-15-67-C-0215 and the National Science Foundation through Grant No. GP-28402.

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[13] R. J. Fitzgerald and G. R. Brubaker, *Inorg. Chem.*, **8**, 2265 (1969).

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Noble Gas–Boron Compounds[1a]

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Almost all theoretical and experimental studies on noble gas compounds relate to oxygen and fluorine chemistry.[2] Recently, however, there has been an increased interest in compounds containing noble gas–chlorine,[3] –bromine,[4] and –nitrogen[5] bonds. It is interesting to note that noble gas–boron compounds had been claimed to exist about 30 years ago,[6a] repudiated,[6b] and, finally, definitively synthesized by an indirect reaction.[6c] We have employed LC (Hartree–Fock) AO-MO-SCF wavefunctions to investigate the potential surfaces of $^1\Sigma$ HeB$^+$, $^1\Sigma$ NeB$^+$ and $^1\Sigma$ ArB$^+$, and we compare our results to previously studied fluorine and nitrogen compounds. Connection is made between the diatomic results and other facets of noble gas and boron chemistry.

Methods of Calculation

The potential surfaces of HeB$^+$, NeB$^+$, and ArB$^+$ were obtained using programs developed in this laboratory.[7] The helium atom was represented by five s-type gaussian basis functions contracted to two basis orbitals,[8] neon and boron were represented by ten s-

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[1] (a) Financial support was provided by the Power Branch of the Office of Naval Research, Contract No. N00014-67-A-0151-0016. (b) NSF Predoctoral Fellow, 1968–1970.

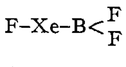
[2] J. F. Liebman and L. C. Allen, *J. Chem. Soc. D*, 1355 (1969); *J. Amer. Chem. Soc.*, **92**, 3539 (1970).

[3] G. J. Perlow and M. R. Perlow, *J. Chem. Phys.*, **41**, 1157 (1964); **48**, 955 (1968).

[4] G. J. Perlow and H. Yoshida, *ibid.*, **49**, 1474 (1968).

[5] W. Kaul and R. Fuchs, *Z. Naturforsch. A*, **15**, 326 (1964); J. F. Liebman and L. C. Allen, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 27 (1971).

[6] (a) H. S. Booth and K. S. Willson, *J. Amer. Chem. Soc.*, **57**, 2273 (1935). (b) E. Wiberg and K. Karbe, *Z. Anorg. Chem.*, **256**, 307 (1948). They also tried to cause Xe and Kr to react with BF$_3$ in the liquid phase but found them almost immiscible. (c) C. T. Goetschel, K. R. Loos, and V. A. Campanile, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1968, No. INOR 213; C. T. Goetschel and K. R. Loos, submitted for publication in *J. Amer. Chem. Soc.* This latter reference gives Raman and ir spectra to prove that the molecule has the structure



$$F{-}Xe{-}B{<}^{F}_{F}$$

Further work by the same authors shows that the krypton compound also possesses this structure.

[7] S. Rothenberg, P. Kollman, M. E. Schwartz, E. F. Hayes, and L. C. Allen, *Int. J. Quantum Chem.*, **3S**, 715 (1970).

[8] J. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

TABLE I[a]

	HeB$^+$			NeB$^+$			ArB^{+c}		
R	E	Δq^b (charge on He)	S^b	E	Δq (charge on Ne)	S	E	Δq (charge on Ar)	S
2	−26.8354	0.15	−0.26	−152.2965	0.115	−0.26	−549.6632	0.4	−0.9256
3	−27.0250	0.084	−0.11	−152.6536	0.1	−0.08	−550.7897	0.4	−0.1428
4	−27.0670	0.024	−0.03	−152.7180	0.04	−0.01	−550.9763	0.2	−0.0381
5	−27.0744	0.005	−0.005	−152.7293	0.01	0.001	−551.0107	0.08	−0.0124
6	−27.0755	0.001	−0.0006	−152.7306	0.002	0.002	−551.0148	0.03	0.0118
∞^d	−27.0757	0	0	−152.7306	0	0	−551.0144	0	0

[a] Distances are in bohrs and the energies are in hartrees in this table and in all discussions. [b] Overlap population. This was determined according to the Mulliken population analysis method. [c] This is without d orbitals on the Ar. A comparative study of the effect of d orbitals at $R = 4$ and $R = \infty$ is shown in Table II. [d] This constitutes separation to the neutral noble gas atom and the B$^+$ ion.

and five p-type gaussians contracted to three s- and one p-type basis orbitals,[9] and argon was represented by seventeen s and twelve p gaussians contracted to four s and three p basis orbitals.[10] Basis sets of this quality have been quite successful in qualitatively describing a considerable range of other chemical phenomena, *e.g.*, hydrogen bonding and rotational barriers. For one point on the ArB$^+$ potential surface ($R = 4a_0$), a single-component d orbital was included in the Ar basis set with its exponent matching $r_{\max}$ of the d function radial distribution to $r_{\max}$ of the p function. This gives a d function exponent twice that for the p. It is also to be noted that while the set of functions [d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{xz}, d_{yz}] is dependent, our programs include all of them thereby increasing the basis set flexibility slightly because $d_{xx} + d_{yy} + d_{zz}$ has s symmetry.[11]

Results and Discussion

Consider the potential curves for $^1\Sigma$ HeB$^+$, NeB$^+$ and ArB$^+$ as represented in Table I for $R = (2, 3, 4, 5 \text{ and } 6)a_0$. The value given for $R = \infty$ is that of the separated species: the noble gas atom and the B$^+$ ion. All curves are repulsive and separate properly into closed-shell species. The rough parallel between a decreasing overlap with increasing separation and the repulsive nature of the potential energy curve is found for these three species.

The charge transfer (*i.e.*, amount of charge on the noble gas atom) decreases monotonically with increasing R and increases monotonically from HeB$^+$ to NeB$^+$ to ArB$^+$. Although one cannot quantitatively correlate Δq with bond strengths (either force constants or dissociation energy), the large charge transfer in ArB$^+$ at intermediate distances ($R = (3\text{–}4)\cdot a_0$) qualitatively suggests the possible stability of XeB$^+$. It is surprising that the charge is almost equally partitioned between Ar and B despite the 7.5-eV difference in ionization potentials. The charge transfer considered here is due to both σ- and π-electron donation from the noble gas atom (except, of course, for He where it can only be σ) to B$^+$. We have included d orbitals (at $R = 4$ and ∞) on the Ar atom to serve as polarization functions for both p_σ and p_π orbitals. As shown in Table II, the change on introducing d orbitals is extremely small (the major effect occurring in the σ orbitals).

TABLE II

EFFECT OF d ORBITALS FOR ArB^{+a}

	Without d function	With d function change	With minus without
E	−550.9763	−550.9815	−0.0052
ε(highest occupied σ orbital)	−0.7797	−0.7762	+0.0035
ε(highest occupied π orbital)	−0.9032	−0.9014	+0.0028
V_{ne}	−1347.4236	−1347.6042	−0.1806
V_{ee}	+223.6723	+223.7776	+0.1053
T	+550.2750	+550.3451	+0.0701
Δq (charge on Ar)	+0.2126	+0.2197	+0.0071
Δq_σ (total charge on Ar in σ orbitals)	+0.1860	+0.1891	+0.0031
Δq_π (total charge on Ar in π_x or π_y orbitals)	+0.0195	+0.0191	−0.0004
Overlap population	−0.0381	−0.0433	−0.0052
S_σ (change in overlap of the highest σ orbital)	−0.4857	−0.5011	−0.0154
S_π (overlap of the highest π orbital)	+0.0287	+0.0282	−0.0005

[a] $R = 4a_0$ without and with a single component d function (exponent 1.3146). The net change in total energy for the isolated Ar atom ($R = \infty$ in this case) is less than 0.001 hartree and the one-electron orbital energies, ε_1, changed even less. All energies are in hartrees.

TABLE III

COMPARISON OF NOBLE GAS FLUORIDES, NITRIDES, AND BORIDES[a]

	$^1\Sigma\ \pi^4$ GF$^+$		$^1\Sigma\ \pi^4$ GN$^+$		$^1\Sigma\ \pi^2$ GN$^+$		$^1\Sigma\ \pi^4$ GB$^+$	
G	r	D	r	D	r	D	r	D
He	2.5	0.053	2	0.203	4	0.001	∞	0
Ne	3.1	0.048	3	0.105	3	0.004	∞	0
Ar	3.5	0.111	...	...	...	...	∞	0

[a] Comparison of the $^1\Sigma$ closed-shell noble gas fluorides, $^1\Sigma$ closed- (π^4) and open- (π^2) shell noble gas nitrides, and $^1\Sigma$ closed-shell noble gas borides. (The values of r are in bohrs; D values are in hartrees.)

The diatomic cations of He, Ne, and Ar with F, N, and B are contrasted in Table III. With the ions HeF$^+$, NeF$^+$, and ArF$^+$ as reference, the nitrogen compounds may be thought of as arising from removal of either the σ electrons or one each for the π_x and π_y and lowering the nuclear charge by 2. The former process costs more energy but produces a more bound species. This is because of the high electronegativity of the ^{1}sp^4 N$^+$ ion produced on separation. Removal of π electrons from the fluorine lessens lone-pair repulsion (π^* occupancy) and explains the greater stability of $^1\Sigma$ HeN$^+$ and $^1\Sigma$ NeN$^+$ relative to $^1\Sigma$ HeF$^+$ and $^1\Sigma$ NeF$^+$; this cannot be the only feature in determining the molecular stability, since boron compounds with no lone-pair repulsion are unbound. Bond stability appears to be related to the ionization potential of the non-noble-gas atom combined with the above lone-pair factor. The ionization

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(9) (a) The s functions were taken from ref 8. (b) The p functions were taken from S. Huzinaga, *ibid.*, **42**, 1239 (1965).

(10) S. Huzinaga, *ibid.*, **50**, 1371 (1969).

(11) If the molecule under consideration does not separate into unique states, the effect of d orbitals is evaluated at the equilibrium separation and at the largest internuclear distance studied.

potential of the He, Ne, and Ar is commensurate with F but much higher than that of N and B, and thus only with F is it possible to have the large energy level splitting associated with strong bonding. The appropriate comparison is the sequence of the $^1\Sigma\ \pi^4$ fluorides, $^1\Sigma\ \pi^2$ nitrides, and $^1\Sigma\ \pi^4$ borides because they have respectively eight, six, and four π (and π^*) electrons. (The alternate sequence using the $^1\Sigma\ \pi^4$ nitrides would be out of place, since there are also eight electrons in this case.)

Although HeB^+ is isoelectronic to HB and HeBe, NeB^+ to FB and NeBe, and ArB^+ to ClB and ArBe, the binding energies within each group are quite different. This is easily rationalized by the following considerations. For a crude estimate the binding energies of HeBe, NeBe, and ArBe may be taken as comparable to that of Be_2 (16 kcal/mol[12]). On the other hand, HB, FB, and ClB have dissociation energies of 58, 181, and 118 kcal/mol,[12] respectively. The wave functions for these species may be schematically written in a valence-

$$\psi(NeB^+) = a_1\varphi(NeB^+) + a_2\varphi(Ne^+B) + a_3\varphi(Ne^{2+}B^-)$$

$$\psi(NeBe) = b_1\varphi(NeBe) + b_2\varphi(Ne^+Be^-) + b_3\varphi(Ne^{2+}Be^-)$$

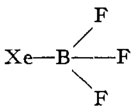
$$\psi(FB) = c_1\varphi(F^-B^+) + c_2\varphi(FB) + c_3\varphi(F^+B^-)$$

bond form. From simple electronegativity arguments, $a_1 \gg a_2 \gg a_3$, $b_1 \gg b_2 \gg b_3$, and $c_2 > c_1 > c_3$. Therefore, the noble gas–boron compounds are *not* analogous to the highly stable boron monohalides but rather to the unbound noble gas beryllium diatomics.[13] The stability of xenon and krypton trifluoroborate has been also rationalized by isoelectronic analogy to ICF_3 and $BrCF_3$.[14] Again this analogy is invalid since

$$\psi(XeBF_3) = d_1\varphi(XeBF_3) + d_2\varphi(Xe^+BF_3^-) + d_3\varphi(Xe^{2+}BF_3^{2-})$$

$$\psi(ICF_3) = e_1\varphi(I^-CF_3^+) + e_2\varphi(ICF_3) + e_3\varphi(I^+CF_3^-)$$

and from ionization potentials $d_1 > d_2 \gg d_3$. But for ICF_3 its known reactions[15] show that $e_2 > e_3 > e_1$. This suggests that xenon trifluoroborate does not have the structural formula[16]



In addition, the charge transfer from the noble gas atom to B^+ in ArB^+ (0.4 at R = 1.6 Å) is sufficient to suggest the potential occurrence of a large inelastic resonant scattering contribution from Ar, Kr, or Xe with B^+ in a crossed-beams experiment. Based on the rough qualitative idea that chemical bonding is associated with charge transfer, one might anticipate XeB^+ to be bound by 10–20 kcal. In spite of this, however, the B–F bond strength is sufficiently high to discourage XeB^+ salt formation, even using the highly stable fluorinated anions SbF_6^-, $Sb_2F_{11}^-$, or PtF_6^-.[17]

Finally, the possibility of ionic salts and other isolable noble gas boron compounds, in addition to the diatomic cations discussed above, is also of interest. We suggest that Xe–B compounds may be synthesized and observed by decomposition of iodoboranes analogous to the synthetic work of Perlow[4] on $XeCl_4$, $XeCl_2$, and $XeBr_2$. Considering the stability of the B_{10} and B_{12} polyhedral cages to oxidative cleavage, a study of $IB_{10}H_9^{2-}$ and $IB_{12}H_{11}^{2-}$ to form the zwitteronic $^+XeB_{10}H_9^{2-}$ and $^+XeB_{12}H_{11}$ (analogous to $^+N_2B_{10}H_8^{2-}N_2^+$, $^+OCB_{10}H_8^{2-}CO^+$) seems desirable. More direct synthesis such as treating various lower boranes with noble gases at low temperatures and/or in a mass spectrometer is another approach.

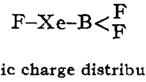
[12] See A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed, Chapman and Hall, London, 1968, for all of the experimental data.

[13] J. F. Liebman, *J. Chem. Educ.*, **48**, 188 (1971).

[14] B.-M. Fung, *J. Phys. Chem.*, **69**, 896 (1965).

[15] This order is rationalized by the alkaline hydrolysis of CF_3I: $CF_3I + KOH \rightarrow CF_3H + KOI$ (an SN2 reaction on I). This indicates the bond polarity is $C^-–I^+$. See H. J. Eméleus, "The Chemistry of Fluorine and Its Compounds," Academic Press, New York, N. Y., 1969, pp 4, 46.

[16] (a) The analysis in this paper was carried out before it was known to us that the correct structure is



$$F\text{–}Xe\text{–}B{<}^{F}_{F}$$

The grossly different electronic charge distribution between ICF_3 and xenon trifluoroborate indicated by the breakdown of isoelectronic analogy leads to the possibility that the atoms may be connected in a different way. However, we make no claim to have anticipated the structure found by Goetschel.[6c] The large number of electrons in this system renders a geometry search economically out of reach at present. (b) A referee has suggested to us that both isomers $XeBF_3$ and $FXeBF_3$ may exist (with different stabilities), require different syntheses, and be unlikely to rearrange.

[17] For example, $XeB^+Sb_2F_{11}^- \rightarrow Xe + BF_2^+SbF_6^- + SbF_3$. However, in $XeB^+SbF_6^- \rightarrow Xe + BF_3 + SbF_3$, the total loss of crystal stability might allow the salt to be metastable.

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Strained Five- and Six-Coordinated Macrocyclic Nickel(II) Complexes[1]

By George A. Kalligeros and Elliott L. Blinn*

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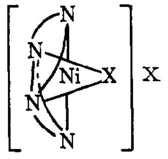
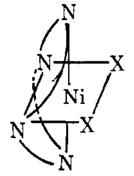
Most of the research on macrocyclic complexes has utilized cyclic tetraamine ligands with at least 13 atoms composing the ring.[2-4] In general, the donor atoms in such complexes are coplanar, and the geometry of the complex is either square planar or trans octahedral. Although little work has been done on the complexes of saturated cyclic tetraamine ligands, it is already known that the 14-membered macrocycle 1,4,8,11-tetraazacyclotetradecane, cyclam, forms a trans octahedral complex with the nickel(II) ion.[5]

Models of 12-membered saturated cyclic tetraamines suggest that the small ring size does not permit coplanar coordination of the four nitrogen atoms in the macrocycle, but such a ligand can be coordinated around the face of either a trigonal-bipyramidal structure (I) or an octahedral structure (II). Two studies of the 12-



I



II

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[1] Paper presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

[2] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

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[4] D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius, Alfred Werner*, 174 (1967).

[5] B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).