We consider, finally, the "metal–metal" force constant, which, at ~1 mdyn/Å, is sizable. In fact it is slightly larger than in $Bi_6(OH)_{12}^{6+}$.[9a] For both $M_6O_{19}^{8-}$ and $Bi_6(OH)_{12}^{6+}$ the set of "metal–metal" coordinates is kinetically equivalent to the set of cage angles α and γ. In both cases the "metal–metal" coordinate is the main contributor to the lowest frequency A_{1g} fundamental. However while this fundamental gives the strongest Raman band in the $Bi_6(OH)_{12}^{6+}$ spectrum, it gives one of the weakest for $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$. In the Wolkenstein bond polarizability theory,[15] Raman intensity for totally symmetric vibrations of isotropic molecules arises exclusively from the stretching of bonds; bond bending does not contribute. This assumption has been tested experimentally and holds rather well.[16–18] The low intensity observed for the M_6 breathing mode for the $M_6O_{19}^{8-}$ species can be attributed to the small admixture of bridge and central oxygen stretching. The high intensity observed for $Bi_6(OH)_{12}^{6+}$, on the other hand, suggests that metal–metal interaction is significant.

It does not follow, however, that the "metal–metal" force constant for $Bi_6(OH)_{12}^{6+}$, 0.97 mdyn/Å,[9a] is a realistic reflection of the strength of the interaction. The present study shows that one can obtain force constants of this magnitude without any metal–metal interaction. The restoring force arises from the kinetically equivalent set of cage deformations. No doubt this is the case for $Bi_6(OH)_{12}^{6+}$ as well, since it seems highly unlikely that the Bi–Bi "bond" could be as strong as the metal–metal bonds in $Re_2(CO)_{10}$ or $Mn_2(CO)_{10}$, for which the metal–metal force constants are 0.82 and 0.59 mdyn/Å, respectively.[19] These considerations emphasize the primacy of Raman intensities over vibrational frequencies in any discussion of metal–metal bonding in polynuclear complexes with bridging ligands.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH AND NUCLEAR CHEMISTRY DIVISIONS OF THE LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA 94720

Nitrogen 1s Electron Binding Energies. Correlations with Molecular Orbital Calculated Nitrogen Charges

BY DAVID N. HENDRICKSON,[1] JACK M. HOLLANDER,[2] AND WILLIAM L. JOLLY[1]

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Nitrogen 1s electron binding energies are given for 56 nitrogen compounds. Correlations are observed between these measured binding energies and nitrogen atom charges calculated from either CNDO or extended Hückel molecular orbitals. The molecular structure of the oxyhyponitrite ion ($N_2O_3^{2-}$) and the bonding characteristics of various metal-coordinated ligands are investigated by means of these correlations.

Introduction

Extensive studies of chemical shifts associated with atomic core electron binding energies have been made by Siegbahn *et al.*,[3] by use of the relatively new technique X-ray photoelectron spectroscopy. Measured binding energies have been correlated with formal oxidation states and with fractional atomic charges calculated by a modification of Pauling's method. We have recently reported preliminary results of a study of solid nitrogen compounds by X-ray photoelectron spectroscopy, and we have shown that the nitrogen 1s binding energies can be correlated with nitrogen atomic charges calculated from CNDO molecular orbital eigenfunctions.[4]

In this paper we extend the correlation of the nitrogen 1s binding energy data to include atomic charges evaluated by the extended Hückel molecular orbital method. We use these correlations and the observed nitrogen 1s binding energies for sodium oxyhyponitrite ($Na_2N_2O_3$) to establish the structure of the $N_2O_3^{2-}$ ion. In addition, we use binding energy data for some nitrogen-containing metal-coordinated ligands to characterize the bonding in these ligands.

Experimental Section

Mg Kα X-radiation (1253.6 eV) was used. The kinetic energy of the photoelectrons was measured in an iron-free, double-focusing magnetic spectrometer[5] shown schematically in Figure 1. The instrumental line width, including the contribution from the X-ray line, was about 1 eV, and the observed photoelectron lines had widths of 1.5–2.5 eV. Photoelectrons were counted[6] typi-

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(1) Department of Chemistry, University of California, and Inorganic Materials Research Division, Lawrence Radiation Laboratory, Berkeley, Calif.

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(3) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, "ESCA Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells AB, Uppsala, 1967.

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(6) A Bendiz curved channel multiplier ("Channeltron") was used as the electron detector.

cally for time intervals of 12 sec at each magnetic field setting, and the spectrometer current in the range 1.0–1.5 A was varied in increments of 0.2 mA.

The compounds studied were either purchased or prepared by standard syntheses. Spectrometer samples were prepared by brushing the powdered material onto double-faced conducting tape attached to an aluminum plate that served as a heat and electron sink. Three measurements were made for each sample; in each case the carbon 1s line (arising from pump oil which forms a film on the samples) was recorded. The film of pump oil provides a convenient reference peak and probably also acts to remove surface charging that may arise with insulating samples. By this method it is possible to locate the photoelectron peaks reproducibly to within 0.2 eV.

The work function for the spectrometer material (aluminum) was assigned the value 4.0 eV. This normalization gives the best agreement of our nitrogen core electron binding energies with previously measured values for the same nitrogen compounds and makes it possible to include some of the binding energies of Siegbahn, *et al.*,[3] in the correlations with our calculated charges.

Calculations

Molecular orbital eigenfunctions were obtained from CNDO[7] and extended Hückel[8] calculations. In both cases computations were performed with a CDC 6400 computer using a Fortran IV program. Calculational details and required input data for the CNDO calculations are given in ref 7. In the extended Hückel calculations, the Coulomb integrals, H_{ii}, were approximated by the valence state ionization potentials calculated by Hinze and Jaffé.[9] The arithmetic mean approximation for the off-diagonal elements of the H matrix

$$H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$$

was used.[10] Here S_{ij} is the overlap integral between the ith and jth orbitals.

Net atomic charges were obtained by subjecting the extended Hückel molecular orbitals to a Mulliken population analysis.[11] In the CNDO method there is no overlap population, and as such the net atomic charges are easily obtained from the appropriate diagonal elements of the charge density matrix.

Cartesian coordinates for complicated systems were obtained from program PROXYZ,[12] coupled with experimental[13] or estimated molecular parameters.

Theory

Because we are dealing with measurements on solid materials, the calculated electron-binding energies are referred to the Fermi levels of the solids. We calculate the electron-binding energies, E_b, from the relation[3]

$$E_b = E_{\text{X-ray}} - E_{\text{kin}} - \phi_{\text{spec}}$$

where $E_{\text{X-ray}}$ is the incident X-ray energy, E_{kin} is the kinetic energy of the photoelectron, and ϕ_{spec} is the work function of the spectrometer material, aluminum. The correlectron binding energies are dependent on the chemical environment, and previous discussions have shown that they are principally determined by the potential associated with the valence shell electron density and the crystal field by the core electrons.[3,14]

For binary salts, Siegbahn and coworkers[3,14] have formulated a relation between the electronic charge (q) removed from the valence shell of an atom and the energy shift (ΔE) of the core electrons of that atom

$$\Delta E = \left(\frac{1}{r} - \frac{\alpha}{R}\right)q$$

Here r is the radius of the valence shell, and α is the contribution to the Madelung constant from the atom at the internuclear distance R. A relation is expected between the measured binding energy and the valence charge density.

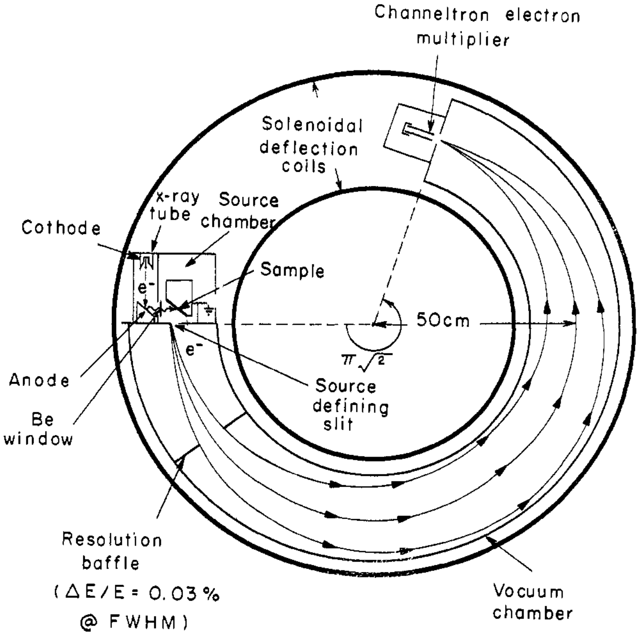

Figure 1.—Schematic illustration of the experimental setup.

Results and Discussion

Correlation with Atomic Charges.—Extended Hückel calculations were completed for 28 nitrogen compounds; the calculated nitrogen atom charges and the measured nitrogen 1s binding energies are listed in Table I. Some binding energies determined in previous studies are also given with the corresponding calculated nitrogen charges. A linear correlation between 1s nitrogen binding energies and extended Hückel calculated nitrogen charges is demonstrated in Figure 2.

The range of nitrogen 1s binding energies covered by this correlation plot is approximately 10 eV, extending from the nitrate ion to pyridine. This is

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[7] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129, S136 (1965). A modified CNDO/1 version involving empircally evaluated repulsion integrals was used, as per P. M. Kuznesof and D. F. Shriver, *J. Am. Chem. Soc.*, **90**, 1683 (1968).

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[9] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

[10] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[11] R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2388, 2343 (1955).

[12] P. M. Kuznesof, Quantum Chemistry Program Exchange, Indiana University, QCPE 94, 1966.

[13] "Table of Interatomic Distances," L. E. Sutton, Ed., Special Publication No. 11, The Chemical Society, London, 1958, and No. 18, Supplement, 1965.

[14] R. Nordberg, R. G. Albridge, T. Bergmark, U. Ericson, J. Hedman, C. Nordling, K. Siegbahn, and B. J. Lindberg, *Arkiv Kemi*, **28**, 257 (1968).

about the same range covered by Nordberg, *et al.*,[14] in their correlation of nitrogen 1s binding energy with fractional atomic charge calculated by a modification of Pauling's method. In the case of our extended Hückel plot the correlation seems to be linear, whereas the correlation obtained by Nordberg, *et al.*, shows curvature. In addition, the extended Hückel calculations assign charges to the nitrogens in *n*-amyl nitrite, nitrite ion, cyanide ion, and azide ion that fit reasonably well on the line, whereas their fit on the modified Pauling plot is poor. It will be noted that the extended Hückel calculations give reasonably good fit for nitrogen molecules that contain sulfur or phosphorus atoms. In these cases it was found (see Table I) that inclusion of 3d orbitals on the sulfur or phosphorus atoms did not appreciably change the calculated nitrogen atom charges.

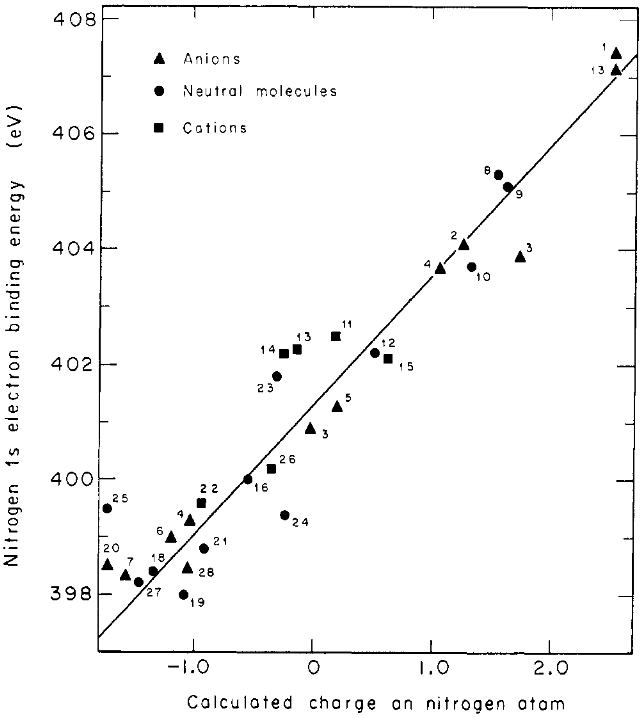


Figure 2.—Plot of nitrogen 1s binding energies *vs.* extended Hücke calculated charges on nitrogen atoms.

TABLE I

NITROGEN 1s BINDING ENERGIES AND CALCULATED CHARGES

Compound no.	Compound	Binding energy, eV	Calcd nitrogen atom charge CNDO	Extended Hückel[g]
1	$NaNO_3$	407.4	+0.429	+2.557
2	$NaNO_2$	404.1	+0.100	+1.273
3	$Na_2(ON\mathbf{N}O_2)$	403.9	+0.140	+1.749
3	$Na_2(O\mathbf{N}NO_2)$	400.9	−0.195	−0.090
4	$Na(N\mathbf{N}N)$	403.7	+0.096	+1.066
4	$Na(\mathbf{N}N\mathbf{N})$	399.3	−0.548	−1.033
5	$Na_2N_2O_2$	401.3	−0.256	+0.175
6	KCN	399.0	−0.518	−1.181
7	KOCN	398.3	−0.550	−1.572
8	*p*-$HOC_6H_4NO_2$	405.3[a]	+0.353	+1.541
9	$C_6H_5NO_2$	405.1[a]	+0.347	+1.613
10	*n*-$C_5H_{11}ONO$	403.7[a]	+0.288[b]	+1.323[b]
11	$N_2H_6SO_4$	402.5	+0.094	+0.184
12	$(CH_3)_3NO$	402.2[a]	+0.079	+0.520
13	$\mathbf{N}H_4NO_3$	402.3	+0.039	−0.145
13	$NH_4\mathbf{N}O_3$	407.2	+0.429	+2.557
14	$(CH_3)_4NB_3H_8$	402.2	+0.185	−0.253
15	NH_3OHCl	402.1	+0.219	+0.612
16	$(CONH_2)_2$	400.0	−0.133	−0.550
17	$(NH_2)_2CNCN$	399.2 br	−0.17 to −0.31[c]	−0.71 to −1.56[c]
18	C_6H_5CN	398.4[a]	−0.226	−1.356
19	C_5H_5N	398.0[a]	−0.166	−1.098
20	KSCN	398.5		−1.672 (−1.711)
21	$NH_3(s)$	398.8	−0.079	−0.914
22	S_4N_3Cl	399.6		−0.912, −1.03[d] (−0.915, −0.984)
23	NH_3SO_3	401.8		−0.262 (−0.307)
24	$C_6H_5CONH_2$	399.4	−0.238	−0.236
25	$(NPCl_2)_3$	399.5		−1.718 (−1.741)
26	$C_5H_5N \cdot HCl$	400.2	+0.035	−0.352
27	BN	398.2		−1.4[f]
28	$Na_3(PO_2NH)_3$	398.5		−0.971 (−1.058)[e]

[a] Data of Siegbahn, *et al.*[3] [b] Charge calculated for CH_3ONO, the structure of which is known. [c] The four structurally different nitrogen atoms of this molecule bear different calculated charges. [d] There are two structurally different nitrogen atoms. [e] Calculated r_{N-P} = 1.50 Å. [f] Treated approximately; see Results and Discussion. [g] Number in parentheses is for the case where 3d orbitals are included.

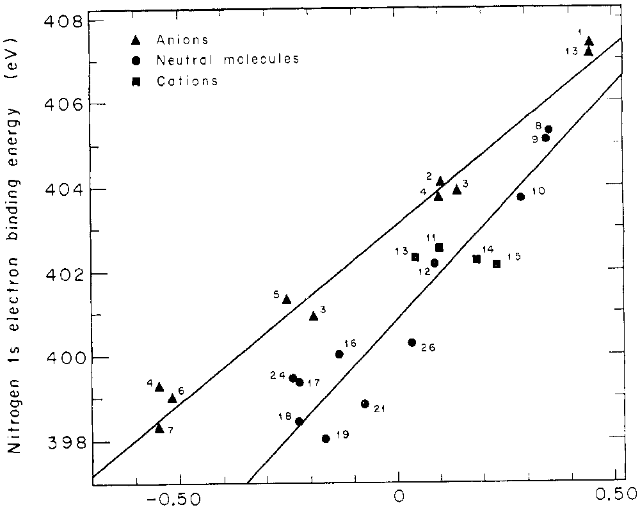
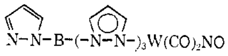


Figure 3.—Plot of nitrogen 1s binding energies *vs.* CNDO-calculated charges on nitrogen atoms.

There are qualifications that need be stated regarding two of the compounds. In the case of boron nitride the graphite-like structure was only approximated; only 24 atoms were considered in calculating the charge on a central nitrogen atom. The crystal structure of compound **28**, $Na_3(PO_2NH)_3$, has not been reported; we assumed a cyclic anion with the bond distances r_{N-H} = 1.0 Å and r_{P-O} = 1.5 Å, coupled with two different P-N distances, 1.5 and 1.7 Å (*cf.* 1.65 Å for r_{P-N} in $(NPCl_2)_3$[13]). The calculations of the nitrogen charges gave for these two cases −0.971 and −0.984, respectively (without considering 3d orbitals on the phosphorus atoms).

The nitrogen charges obtained from the extended Hückel calculations range from −1.7 to almost +2.6. This range is to be contrasted with the much smaller charge range calculated from the CNDO molecular orbitals which were obtained for the same molecules (see Table I). As noted earlier,[4] the CNDO correlation plot (Figure 3) shows two lines—one characteristic of anions and the other characteristic of neutral molecules and possibly cations. Two rationalizations can be formulated: (a) the two lines are merely an artifact of the CNDO method due to an inherent overemphasis of electron repulsion in the CNDO calculations of

TABLE II
NITROGEN 1s BINDING ENERGIES

Compound no.	Compound	Binding energy, eV
29	$[Rh(NH_3)_6](NO_3)_3$	407.3
30	*trans*-$[Co(en)_2(NO_2)_2]NO_3$	406.8
31	*p*-$NO_2C_6H_4CONH_2$	405.9
32	$[Rh(NH_3)_5NO_2]Br_2$	404.4
33	$Co(NH_3)_3(NO_2)_3$	404.1
34	$[Co(NH_3)_5NO_2]Cl_2$	404.0
35	$K[Co(NH_3)_2(NO_2)_4]$	404.0
36	$K_3Co(NO_2)_6$	404.0[a]
37	*trans*-$[Co(NH_3)_4(NO_2)_2]SO_4$	403.9
30	*trans*-$[Co(en)_2(NO_2)_2]NO_3$	403.8
38	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	403.3
39	S_4N_4	402.1
40	$[Co(NH_3)_5NO]Cl_2$	402.0
41	$C_6H_5NH_2NH_2\cdot HCl$	401.4[b]
42	$K_3[Cr(CN)_5NO]$	400.7
29	$[Rh(NH_3)_6](NO_3)_3$	400.7
43	$[Ir(NH_3)_5Cl]Cl_2$	400.6
44	 $N{-}N{-}B{-}({-}N{-}N{-})_3W(CO)_2NO$	400.6[c]
30	*trans*-$[Co(en)_2(NO_2)_2]NO_3$	400.4
32	$[Rh(NH_3)_5NO_2]Br_2$	400.3
45	$S_4N_4\cdot SbCl_5$	400.2
46	S_7NH	400.2
40	$[Co(NH_3)_5NO]Cl_2$	400.2
33	$Co(NH_3)_3(NO_2)_3$	400.2
35	$K[Co(NH_3)_2(NO_2)_4]$	400.0
34	$[Co(NH_3)_5NO_2]Cl_2$	400.0
47	$[Co(NH_3)_6]_2(SO_4)_3$	400.0
48	$[Co(NH_3)_5Cl]Cl_2$	400.0
37	*trans*-$[Co(NH_3)_4(NO_2)_2]SO_4$	399.9
49	$Cr(NH_3)_6Cl_3$	399.9
31	*p*-$NO_2C_6H_5CONH_2$	399.6
50	$S_4N_4H_4$	399.5
51	$(NPCl_2)_4$	399.2
52	$K_3[Cr(CN)_6]$	398.6
42	$K_3[Cr(CN)_5NO]$	398.4
38	$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	398.2
53	P_3N_5	397.8
54	$K_4[Fe(CN)_6]\cdot 3H_2O$	397.6
55	VN	397.2[d]
56	CrN	396.6

[a] A small peak attributable to nitrate impurity was observed at 407.0 eV. [b] Very broad peak. [c] Only one relatively sharp peak observed. [d] A decomposition product peak at 401.0 eV was observed.

anionic molecules; (b) the two lines are an indication of differing lattice potentials associated with a core electron at either an anionic or a neutral site.

It is difficult at this time to indicate clearly the cause of the two CNDO lines. The fact that the extended Hückel data show no indication of the same behavior can probably only be taken as evidence of the simplicity of the latter calculations, at least insofar as this version of the extended Hückel method is concerned. Previous work by Siegbahn and coworkers has shown that the expected differences in crystal potentials do not appear in the measured values (*i.e.*, S_{2p} binding energies in a series of sulfates). This can also be seen in our N 1s data for the three nitrates, compounds **1**, **13**, and **29**. Even further evidence for this lack of expected lattice potential influence can be seen in the data for the series of nitrocobaltic ammines, compounds **33**, **34**, **35**, **36**, **37**, and **47**. Throughout this series the measured nitrogen 1s binding energy for either the coordinated NH_3 or NO_2^- is approximately constant. There is little evidence of discontinuity in the binding energies at the transition from a neutral to an anionic site.

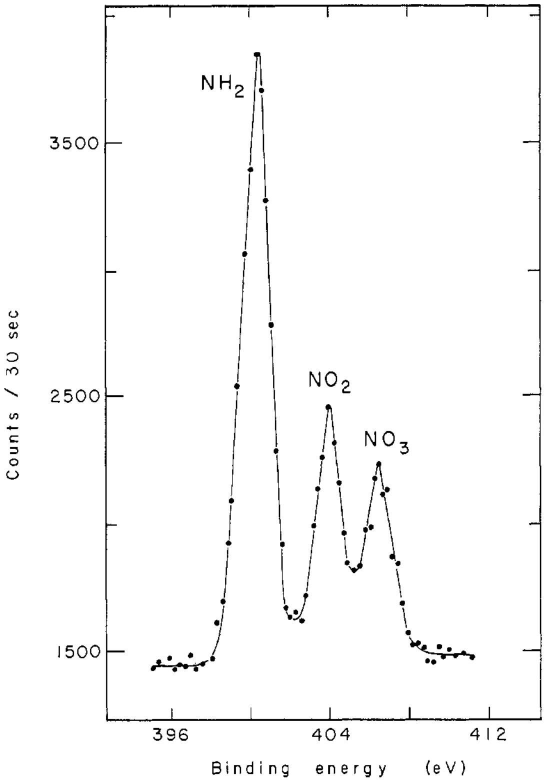


Figure 4.—Nitrogen 1s photoelectron spectrum for *trans*-$[Co(NH_2CH_2CH_2NH_2)_2(NO_2)_2]NO_3$.

Character of Metal-Coordinated Ligands.—The power of the X-ray photoelectron method can be clearly seen in Figure 4, where we give the nitrogen 1s spectrum of *trans*-$[Co(en)_2(NO_2)_2]NO_3$. Measurement of the nitrogen 1s binding energy of various metal-coordinated ligands can give insight into the character of the ligands. The binding energies of some metal-coordinated ammonia groups are listed in Table II. Comparison of these nitrogen-binding energies with those obtained for the free ligand and for the ammonium ion (see Table I) as it exists in NH_4NO_3 shows that coordination of ammonia to Co(III), Rh(III), Ir(III), and Cr(III) gives partial ammonium-like character to the ammonia group. A similar result has been found for the triphenylphosphine ligand; the phosphorus 2p binding energies for coordinated triphenylphosphine and for a phosphonium ion were greater than for free triphenylphosphine.[15]

In the case of the nitro ligand, however, the nitrogen 1s binding energies found for either $NaNO_2$ or for the metal-coordinated nitrite are approximately the same. Probably this can be explained by the metal-to-ligand π back-bonding operative in the metal–nitrite bond. This back-bonding would tend to keep the charge on the nitrogen atom approximately the same in the free

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(15) M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, unpublished data.

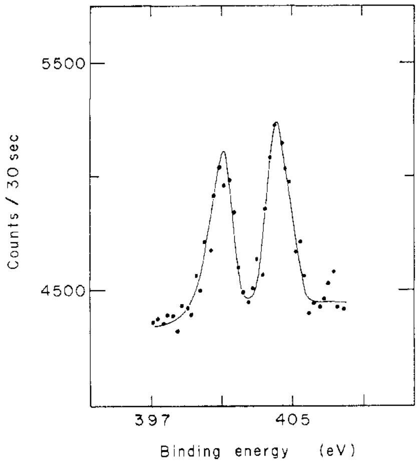


Figure 5.—Nitrogen 1s photoelectron spectrum for $Na_2N_2O_3$. Sodium nitrite impurity accounts for excess area in the higher binding energy peak.

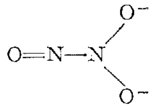
and coordinated ligand. Considering the more extensive back-bonding expected in the metal-coordinated cyanide ion, it is heartening to see that the nitrogen 1s binding energy is appreciably lower for the cyanide coordinated to Fe(III), Cr(I), and Cr(III) than for the "free" cyanide in KCN.

Another problem which can be studied by the X-ray photoelectron method is the determination of the character of the NO group in various metal nitrosyls.[16] There are four possible bonding situations: (a) lone-pair donation to the metal from NO^+; (b) lone-pair donation from NO with the odd electron retained by the NO; (c) lone-pair donation from NO^-; (d) bridge bonding as encountered in metal carbonyl compounds. The majority of metal nitrosyls are believed to be best formulated with the (a) type of bonding.

In Table II are listed the nitrogen 1s binding energies for two metal nitrosyl cyanides, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ and $K_3[Cr(CN)_5NO]\cdot H_2O$. It can be seen that the CN^- peak is relatively invariant to changes in the metal, whereas the NO peak shifts appreciably. This agrees with observations on the infrared spectra of these compounds;[17] that is, the CN stretching frequency is relatively unchanged as opposed to the large change for the NO stretch frequency from 1944 cm^{-1} in the formally Fe(II) compound to 1645 cm^{-1} in the Cr(I) compound.[14] Both of these compounds have been formulated as NO^+ compounds,[17] but their NO nitrogen 1s binding energies clearly show that there is a marked difference in nitrogen charge in these two cases. It is a well-known fact that the NO^+ ligand has an empty π^* orbital available for back-bonding from the metal and further that back-bonding is greater in compounds with metals in lower oxidation states. The lower oxidation state in the case of the Cr(I) compound, indicating greater back-bonding, would be a possible explanation for the apparently less positive NO nitrogen in $Cr(CN)_5NO^{3-}$.

However, consideration of the measured NO binding energy for the formally Co(III) compound, $[Co(NH_3)_5NO]Cl_2$ (black isomer), indicates a certain predicament. This diamagnetic compound has been found to have a monomeric structure,[18] and the Co–N bond distance is reasonable for a Co^{3+} to NO^- bond. The NO nitrogen in this cobalt compound would be expected then to possess the most negative nitrogen charge of these three nitrosyls, but if the binding energies are indicative, the cobalt compound is somewhat intermediate. It should be noted that the Co–N–O bond angle[18] is 180°; this feature is inconsistent with the NO^- formulation but is consistent with a Co^+ to NO^+ bond. Resolution of this problem will be best attained by carrying out more nitrogen binding energy measurements on metal nitrosyls and possibly by studying the effective charges on the metal atoms.

Structure of the Oxyhyponitrite Ion.—Perhaps the most remarkable demonstration in this study of nitrogen compounds is the clear proof of the existence of structurally different nitrogen atoms in the oxyhyponitrite ion, $N_2O_3^{2-}$. Various studies have been undertaken to differentiate between the possible structures of this ion, the three most probable being


I

$O{=}N{-}O{-}N^{-}{-}O^{-}$

II

$^{-}O{-}N{=}N{-}O{-}O^{-}$

III

Addison, *et al.*,[19] concluded that the ultraviolet absorption spectrum of $N_2O_3^{2-}$ indicated an N=N bond. Calorimetric measurements[20] have suggested structure I as most probable, and the infrared spectrum has been interpreted as having bands indicative of an $-NO_2$ grouping.[21] The nitrogen 1s photoelectron spectrum of $Na_2N_2O_3$ (see Figure 5), with two resonances, clearly rules out structure II as a possibility. In order to distinguish between the two remaining structures, CNDO and extended Hückel calculations were completed for the two geometries (varying the N–N bond

TABLE III
CALCULATED NITROGEN CHARGES FOR TWO ASYMMETRIC OXYHYPONITRITE STRUCTURES

	Calculated nitrogen charges[a]			
	CNDO		Extended Hückel	
r_{N-N}, Å	q_1	q_2	q_1	q_2
		Structure I		
1.30	0.133	−0.151	1.75	0.040
1.50	0.147	−0.239	1.75	−0.090
		Structure III		
1.30	−0.158	−0.145	0.288	0.286
1.50	−0.181	−0.188	0.198	0.254

[a] For each molecular orbital method the net nitrogen charges, q_1 and q_2, are given for the two structurally different nitrogen atoms in each structure.

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distance in each case). The net nitrogen charges obtained from the calculations are given in Table III. Structure I is indicated by these calculations; indeed structure III would be predicted to show only one peak, for the two different nitrogens are predicted to have approximately the same charge. Finally it can be seen in Figures 2 and 3 that the points representing structure I do fit the correlation lines. Recently the oxyhyponitrite ion has been shown by asymmetric ^{15}N-labeling to have two structurally different nitrogen atoms.[22]

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Zeeman Studies Including the Molecular *g* Values, Magnetic Susceptibilities, and Molecular Quadrupole Moments in Phosphorus and Nitrogen Trifluorides and Phosphoryl, Thionyl, and Sulfuryl Fluorides

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The high-field and first- and second-order Zeeman effect has been observed in phosphorus trifluoride (PF_3), nitrogen trifluoride (NF_3), phosphoryl fluoride (POF_3), thionyl fluoride (SOF_2), and sulfuryl fluoride (SO_2FO_2). For PF_3 the g values perpendicular and parallel to the molecular symmetry axis are $|g_\perp| = 0.0659 \pm 0.0003$ and $|g_\parallel| = 0.0815 \pm 0.0020$. The average magnetic susceptibility anisotropy is $\chi_\perp - \chi_\parallel = (1.32 \pm 0.20) \times 10^{-6}$ erg/G^2 mol. Using an appropriate choice for the g-value signs gives the quadrupole moment of $Q_\parallel = +(24.1 \pm 3.1) \times 10^{-26}$ esu cm^2. The paramagnetic susceptibilities are $\chi^{p}{}_\perp = 147.9 \pm 1.0$ and $\chi^{p}{}_\parallel = 259.6 \pm 1.0$ in units of 10^{-6} erg/G^2 mol. The anisotropy in the second moments of the electronic charge distributions is $\langle \|^2\rangle - \langle \perp^2\rangle = -(26.6 \pm 0.4) \times 10^{-6}$ cm^2. For POF_3, the values for the perpendicular g value and the magnetic susceptibility anisotropy are $|g_\perp| = 0.0440 \pm 0.0005$ and $\chi_\perp - \chi_\parallel = (1.78 \pm 0.18) \times 10^{-6}$ erg/G^2 mol. Assuming $g_{||} = -0.0815$ as in PF_3 and the negative sign for $g_\perp$ gives the molecular quadrupole moment of $Q_\parallel = (20.4) \times 10^{-26}$ esu cm^2. The paramagnetic susceptibilities are $\chi^{p}{}_\perp = 251.4 \pm 1.0$ and $\chi^{p}{}_\parallel = 245.9 \pm 1.0$ in units of 10^{-6} erg/G^2 mol. The anisotropy in the second moment of the electronic charge distribution is $\langle \|^2\rangle - \langle \perp^2\rangle = -(1.7 \pm 0.4) \times 10^{-16}$ cm^2. For NF_3 the g value perpendicular to the molecular symmetry axis was measured as $g_\perp = -(0.060 \pm 0.001)$. The magnetic susceptibility anisotropy was measured as $\chi_\perp - \chi_\parallel = -(3.0 \pm 1.5) \times 10^{-6}$ erg/G^2 mol. For SOF_2 the g values in the principal inertial axis system are $|g_{aa}| = 0.0802 \pm 0.0070$, $|g_{bb}| = 0.0856 \pm 0.0051$, and $|g_{cc}| = 0.1093 \pm 0.0038$. The magnetic susceptibility anisotropies are $2\chi_{aa} - \chi_{bb} - \chi_{cc} = (0.7 \pm 1.6) \times 10^{-6}$ erg/G^2 mol and $2\chi_{bb} - \chi_{cc} \chi_{aa} = -(1.5 \pm 2.0) \times 10^{-6}$ erg/G^2 mol. Using the negative signs for the g values gives the molecular quadrupole moments of $Q_{aa} = -12.5 \pm 4.5$, $Q_{bb} = -17.0 \pm 4.5$, and $Q_{cc} = 29.5 \pm 5.6$, all in units of 10^{-26} esu cm^2. The diagonal elements in the paramagnetic susceptibility tensor are $\chi^{p}{}_{aa} = 125.0 \pm 2.0$, $\chi^{p}{}_{bb} = 156.9 \pm 2.0$, and $\chi^{p}{}_{cc} = 251.0 \pm 2.0$, all in units of 10^{-6} erg/G^2 mol. The anisotropies in the second moment of the electronic charge distribution are $\langle a^2\rangle - \langle b^2\rangle = (7.7 \pm 1.0) \times 10^{-16}$ cm^2, $\langle b^2\rangle - \langle c^2\rangle = (22.0 \pm 1.2) \times 10^{-16}$ cm^2, and $\langle c^2\rangle - \langle a^2\rangle = -(29.7 \pm 1.3) \times 10^{-16}$ cm^2. For SO_2F_2 the g values in the principal inertial axis system are $|g_{aa}| = 0.0447 \pm 0.0068$, $|g_{bb}| = 0.0456 \pm 0.0015$, and $|g_{cc}| = 0.0565 \pm 0.0009$. The magnetic susceptiblity anisotropies are $2\chi_{aa} - \chi_{bb} - \chi_{cc} = -12.6 \pm 2.6$ and $2\chi_{bb} - \chi_{cc} - \chi_{aa} = 13.2 \pm 3.5$, both in units of 10^{-6} erg/G^2 mol. Using the negative g-value signs gives the molecular quadrupole moments of $Q_{aa} = 3.9 \pm 5.3$, $Q_{bb} = -9.7 \pm 4.6$, and $Q_{cc} = 5.9 \pm 5.9$, all in units of 10^{-26} esu cm^2. The diagonal elements of the paramagnetic susceptibility tensor are $\chi^{p}{}_{aa} = 221.6 \pm 3.1$, $\chi^{p}{}_{bb} = 227.4 \pm 1.0$, and $\chi^{p}{}_{cc} = 226.4 \pm 1.0$, all in units of 10^{-6} erg/G^2 mol. The anisotropies in the second moment of the electronic charge distribution are $\langle a^2\rangle - \langle b^2\rangle = -0.6 \pm 1.4$, $\langle b^2\rangle - \langle c^2\rangle = 0.8 \pm 1.1$, and $\langle c^2\rangle - \langle a^2\rangle = -0.2 \pm 1.5$, all in units of 10^{-16} cm^2.

I. Introduction

Phosphorus trifluoride (PF_3), nitrogen trifluoride (NF_3), phosphoryl fluoride (OPF_3), thionyl fluoride (SOF_2) and sulfuryl fluoride (SO_2F_2) are all similar inorganic molecules. A comparison of the charge distribution, obtained from the molecular quadrupole moments, would be of considerable interest. Microwave spectroscopy has recently been developed as an effective method of determining molecular quadrupole moments and electronic charge anisotropies.[1,2] This method, which has been applied to several molecules,[3] involves the measurement of both the *first-* and *second-*order magnetic field effects. The first-order Zeeman effect gives the molecular magnetic rotational moments or molecular g values. The second-order Zeeman effect gives the anisotropies in the magnetic susceptibilities. The combination of the first- and second-

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