

essentially unchanged, but at 700° the structure slowly degenerates to a brittle pseudo-fibrous form of enstatite. The fluoride-substituted materials are somewhat more thermally stable, retaining their properties well at 920°.

Chemically the fibers are very resistant to hot con-

centrated base, but are slowly attacked by acid. In a study of the nature of acid-treated fiber, essentially no change was found in the stoichiometry of treated batts, indicating that the entire silicate structure is taken into solution. Table III gives some of the properties which have been determined.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASSACHUSETTS

A Test of the Mulliken-Wolfsberg-Helmholz LCAO-MO Treatment of Metal Complexes^{1a}

BY F. A. COTTON^{1b} AND T. E. HAAS^{1c}

Received February 24, 1964

The d-orbital splittings in $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$, and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ have been calculated by the type of LCAO-MO treatment originally suggested by Mulliken and first applied to complexes by Wolfsberg and Helmholz. The calculations were made in order to determine whether good results could be obtained for a variety of systems by adhering to a fixed set of rules for the choice of atomic orbital energies and a fixed value for the proportionality constant relating resonance integrals, H_{ij} , to the product of the overlap integral, S_{ij} , and the geometric mean of the integrals, H_{ii} and H_{jj} . The results show that strict adherence to such rules failed to afford uniformly accurate results.

Introduction

A reliable semiempirical method of calculating orbital energies for complexes of transition metals is obviously greatly to be desired. Two possible avenues to such a method have been proposed and utilized in individual instances, but their general reliability and applicability remain to be tested. The first of these is the point charge (or point dipole) electrostatic model. Some recent examples of its elaboration and use are provided by the work of Maki² and of Fenske, Martin, and Ruedenberg.³ Because a model which treats ligand atoms as point charges is devoid of physical validity,⁴⁻⁶ we do not believe that further studies of it offer promise of ultimate success.

The second approach utilizes the LCAO-MO method implemented by the assumptions of (1) a proportionality between resonance integrals and overlap integrals and (2) the equality of coulomb integrals and the corresponding valence state ionization potentials (VSIP) of atoms. The essentials of this approach were first introduced by Mulliken⁷ and reduced to practice for some transition metal complexes by Wolfsberg and Helmholz.⁸ The rationale and procedures for using VSIP's have been given by Moffitt.⁹

In the past few years several interesting applications of the Mulliken-Wolfsberg-Helmholz (MWH)

method have been reported.¹⁰ One which very clearly exemplifies the *modus operandi* and also gives excellent results is Ballhausen and Gray's treatment of vanadyl complexes.¹¹ However, the question naturally arises whether the treatment can be extended, unmodified, to other systems with comparable success. Especially interesting is whether the proportionality constant appearing in the relationship between overlap integrals and resonance integrals can be kept the same for various metal ions (say, all those of the first transition series) or whether it will be necessary to make what might be euphemistically called "judicious adjustments" from case to case. Specifically, we have formulated these questions: (1) How accurately can orbital energy differences be calculated using the MWH method *without* any *ad hoc* adjusting of either the VSIP's or the proportionality constant in the relationship between overlap integrals and resonance integrals? (2) How sensitive are the results to variations in these parameters?

Our attempt to answer these questions has consisted of the computation of Δ values for several $[\text{M}(\text{NH}_3)_6]^{n+}$ complexes and comparison of the results with the experimentally known Δ values. This sort of problem is one of the simplest and most important and should therefore constitute a fair and minimum test of the value of the method.

Procedure

The complexes selected for treatment are $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$, and $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Ammines were chosen so that metal-ligand π interactions could be ignored. Metal ions of the first transition series were selected because

(1) (a) Supported by the U. S. Atomic Energy Commission. (b) Fellow of the Alfred P. Sloan Foundation. (c) National Science Foundation Pre-doctoral Fellow.

(2) G. Maki, *J. Chem. Phys.*, **28**, 651 (1958); **29**, 162 (1958).

(3) R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).

(4) W. H. Kleiner, *J. Chem. Phys.*, **20**, 1784 (1952).

(5) A. J. Freeman and R. E. Watson, *Phys. Rev.*, **120**, 1254 (1960).

(6) F. A. Cotton, *J. Chem. Educ.*, in press.

(7) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949).

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

(9) W. Moffitt, *Rept. Progr. Phys.*, **17**, 173 (1954).

(10) Citation and discussion of most of these will be found in the Ph.D. Thesis of T. E. Haas, M.I.T., 1963.

(11) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

of the availability of good SCF wave functions and because spin-orbit interactions, which cannot be easily dealt with in the MWH method, are rather small. Finally, the examples used cover a range of d-orbital populations and both of the common transition metal ion oxidation numbers.

Internuclear distances necessary for the calculation of overlap integrals were obtained from the Chemical Society tabulation,¹² either for the salts of the ions in question or for related ones. The values used were 2.00 Å. for the Cr(III)-N distance, 2.00 Å. for the Co(III)-N distance, and 2.15 Å. for the Ni(II)-N distance. (The Co(II)-N distance was estimated to be the same as the Ni(II)-N distance. Variations of a few hundredths of an Ångstrom unit will not significantly affect the results as they are much more sensitive to changes in the wave functions.) The Watson SCF wave functions for the neutral atoms¹³ were used for the metals. As Watson gives no 4p wave functions, these had to be estimated. For the chromium and two cobalt complexes these were assumed to have the same radial dependence as the 4s functions. The calculations on these complexes began before the appearance of some better estimates by Richardson, *et al.*,¹⁴ but for the nickel complex, the latter 4p wave function was used. An analytic expression for the nitrogen wave function was obtained from the tabular data of Hartree¹⁵ by the method of Löwdin.¹⁶ The appropriate combination for an sp^3 hybrid was then taken, and the overlap integrals were calculated by conventional procedures.

The diagonal elements used for the metal atoms were the VSIP, which were simply calculated from the valence state energies given by Skinner and Sumner.¹⁷ Due to the lack of atomic spectral data for terms arising from configurations of the type $3d^n4s4p$, only the 3d and 4s VSIP could be determined. The 4p VSIP were estimated to lie 4 e.v., or 32,360 cm^{-1} , above the 4s VSIP. (This approximation appears to have been used by Ballhausen and Gray,¹¹ although they did not mention it. It is not critical for this work, as we are primarily interested in the MO's arising from the 3d orbitals. It would be of importance in an investigation of charge-transfer spectra.) Another necessary assumption concerning the metal diagonal elements was that all orbital energies had the same charge dependence, which was equal to that of the ground state ionization potential. This assumption was again forced upon us by the limitations of the atomic spectral data. In the one case where sufficient data were available, the charge dependence of the VSIP for copper 3d, 4s, and 4p orbitals was found to be the same and equal to that of the ground state ionization potential (IP) within about 15%.

The dependence of results upon the choice of the ammonia diagonal elements is one of the points for this investigation. Some forethought on the problem will, however, give a strong indication of the proper course to take. The idea behind the use of VSIP is that these energies represent the average energies of the several atomic orbitals in the (nonstationary) excited states in which the atoms are ready to interact. Clearly the valence state concept will give a good description of the metal atom undergoing complex formation in the gas phase. But we are not concerned with the reaction of a nitrogen atom; rather we have to deal with an ammonia molecule. Thus, the energies of the diagonal elements are more appropriately related to molecular properties than to atomic properties. This change is in fact more in keeping with the spirit of the valence state concept than is blind adherence to the use of atomic valence states. The latter would of course be appropriate in the treatment of the formation of ammonia from nitrogen and hydrogen.

Despite the fact that there are strong reasons for preferring the

use of ammonia IP to the use of the nitrogen VSIP as the diagonal element for the ligands in these calculations, a comparison of the results from both these choices should be made. The method is, after all, empirical, and if the VSIP were to give better results, it would certainly be justified to use them, despite the arguments of the previous paragraph.

The general lack of precise data on molecular energy levels would doom an attempt to derive "molecular VSIP" to failure. An alternate procedure would be to use simply the normal ionization potentials for the various ligands, or compounds as closely related to them as possible. This of course is what Wolfsberg and Helmholz did, and what will be done here. The diagonal element for the ammonia molecule will accordingly be taken to be 10.52 e.v., or 84,850 cm^{-1} . This value was determined by electron impact and has been interpreted as being the ionization potential of one of the lone-pair electrons,¹⁸ which is exactly what is required. The question of the charge dependence of this number remains open, as only the first IP is known. Clearly there must be some dependence of the energy of the lone-pair electrons on the amount of charge on the molecule, but how much is difficult to assess. It should presumably be less than the dependence of the VSIP for the bare nitrogen atom, as the protons on the ammonia molecule can help accommodate some of the excess charge. Calculations were therefore carried out for several different assumed values of the charge dependence and will be compared below.

Calculations were also carried out with several different values of the proportionality constant, F , defined in eq. 1, for each compound. Overlap integrals, diagonal elements, and charge

$$H_{ij} = F(H_{ii}H_{jj})^{1/2}S_{ij} \quad (1)$$

dependences for the metal atoms were the same for all of the calculations and are given in Table I. Initially, a charge distribution was assumed and after one cycle of calculation, a charge distribution was calculated, using Mulliken's suggestion¹⁹ that the overlap population be divided equally between the bonded atoms. The calculation was then repeated and this procedure iterated until the assumed and calculated charge distributions agreed to within ± 0.01 unit. The calculations were carried out on the IBM 7090 computer at the M.I.T. Computation Center,

TABLE I
PARAMETERS FOR CALCULATIONS OF ENERGY LEVELS OF
[M(NH₃)₆]ⁿ⁺

Metal	Overlap integrals	Orbital	VSIP, cm^{-1}	Change in VSIP per unit of charge, cm^{-1}
Cr(III)	$G(A_{1g}) = 0.762$	4s	-48,960	-78,500
	$G(E_g) = 0.256$	3d	-57,110	-78,500
	$G(T_{1u}) = 0.475$	4p	-16,700	-78,500
Co(III)	$G(A_{1g}) = 0.754$	4s	-45,650	-87,190
	$G(E_g) = 0.180$	3d	-63,250	-87,190
	$G(T_{1u}) = 0.440$	4p	-13,390	-87,190
Co(II)	$G(A_{1g}) = 0.750$	4s	-45,650	-87,190
	$G(E_g) = 0.149$	3d	-63,250	-87,190
	$G(T_{1u}) = 0.424$	4p	-13,390	-87,190
Ni(II)	$G(A_{1g}) = 0.657$	4s	-58,770	-84,850
	$G(E_g) = 0.137$	3d	-74,530	-84,850
	$G(T_{1u}) = 0.461$	4p	-26,510	-84,850

Results

A schematic representation of the energy level diagram for an octahedral complex is given in Fig. 1. The orbitals are labeled by their symmetry designations, using lower case letters to differentiate the orbitals from crystal field states, which are convention-

(12) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(13) R. E. Watson, *Phys. Rev.*, **119**, 1934 (1960).

(14) J. W. Richardson, W. C. Nieuwpoort, and R. R. Powell, *J. Chem. Phys.*, **38**, 796 (1963).

(15) D. R. Hartree, "The Calculation of Atomic Structures," John Wiley and Sons, New York, N. Y., 1957, pp. 169-173, and references cited therein.

(16) P. O. Löwdin, *Phys. Rev.*, **90**, 120 (1953).

(17) H. A. Skinner and F. H. Sumner, *J. Inorg. Nucl. Chem.*, **4**, 245 (1957).

(18) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, New York, N. Y., 1957, pp. 67-68.

(19) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

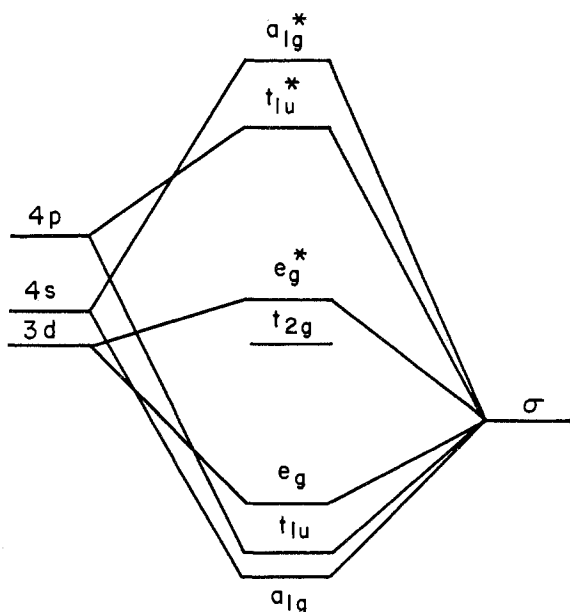


Fig. 1.—A schematic representation of the orbital energies for $[M(\text{NH}_3)_6]$ systems.

ally denoted by the upper case symbols. An asterisk is used to indicate antibonding orbitals. The t_{2g} orbitals are the nonbonding d_{xy} , d_{xz} , d_{yz} set.

In order to compare the effect of choosing the molecular ionization potentials *vs.* nitrogen VSIP, the charge dependence of the former must first be settled. Calculations were carried out using values for the charge dependence ΔIP of $-50,000$, $-84,000$, and $-121,000$ cm.^{-1} . The largest of these was the ΔIP for the nitrogen VSIP, and the others were chosen arbitrarily to cover a reasonable range. The resulting Δ and self-consistent charge q on the central metal atom are presented in Table II. Calculations were made using $F = 2.00$ and $F = 1.82$.

TABLE II
EFFECT OF VARYING CHARGE DEPENDENCE OF AMMONIA IP

Complex	F	$\Delta\text{IP, cm.}^{-1}$	q	$\Delta, \text{cm.}^{-1}$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	1.82	-50,000	0.410	20,550
		-84,000	0.506	21,470
		-121,000	0.602	22,470
	2.00	-50,000	0.356	24,050
		-84,000	0.449	25,340
		-121,000	0.535	26,540
$[\text{Co}(\text{NH}_3)_6]^{3+}$	1.82	-50,000	0.388	14,240
		-84,000	0.486	14,520
		-121,000	0.590	15,090
	2.00	-50,000	0.348	16,450
		-84,000	0.442	16,920
		-121,000	0.538	17,600

From Table II it would appear that the variation of the charge dependence, ΔIP , has its main effect on the calculated charge distribution, and relatively little effect on the splitting parameter Δ . As the criterion to be applied is the correctness of Δ , it would then be justifiable to make a choice among these different values of ΔIP . The one chosen for subsequent use as the ΔIP for ammonia was $-84,000$ cm.^{-1} . This

choice implies approximately 30% delocalization of the net charge on the bound ammonia onto the hydrogens, which seems reasonable.

We are now in a position to compare the results obtained when the ammonia IP and the nitrogen VSIP, respectively, are used in the calculations of the energy levels. Calculations were made for $F = 2.00$ and $F = 1.82$ for each of the ions under study. The results are presented in Table III.

TABLE III
COMPARATIVE EFFECTS OF USING THE AMMONIA IP AND THE NITROGEN VSIP ON THE VALUE OF Δ

Complex	F	N diagonal element	q	$\Delta, \text{cm.}^{-1}$
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	1.82	NH_3 IP	0.506	21,470
		N VSIP	0.884	25,350
	2.00	NH_3 IP	0.449	25,340
		N VSIP	0.793	30,150
$[\text{Co}(\text{NH}_3)_6]^{3+}$	1.82	NH_3 IP	0.486	14,520
		N VSIP	0.870	15,880
	2.00	NH_3 IP	0.442	16,920
		N VSIP	0.792	18,720
$[\text{Co}(\text{NH}_3)_6]^{2+}$	1.82	NH_3 IP	0.366	9,720
		N VSIP	0.668	9,220
	2.00	NH_3 IP	0.320	11,060
		N VSIP	0.593	10,910
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	1.82	NH_3 IP	0.257	8,580
		N VSIP	0.578	7,990
	2.00	NH_3 IP	0.211	9,750
		N VSIP	0.499	9,510

Some interesting observations can be made on these results. For a given value of F both the magnitude and the per cent difference between the two calculations increase with increasing Δ . For the chromium complex, with by far the largest Δ , the difference between the two calculations is about 20%. For the cobalt(III) complex, the difference is about 10%, and for the two divalent complexes, there is no significant difference between the two results. Indeed, in the latter cases, the VSIP of nitrogen gives slightly smaller Δ values, whereas for the two trivalent complexes, considerably larger Δ values result. It is also necessary to begin comparing the results not only internally, but with the experimentally observed values of Δ . These are²⁰: for $[\text{Cr}(\text{NH}_3)_6]^{3+}$, 21,500 cm.^{-1} ; for $[\text{Co}(\text{NH}_3)_6]^{3+}$, 23,500 cm.^{-1} ; for $[\text{Co}(\text{NH}_3)_6]^{2+}$, 10,500 cm.^{-1} ; and for $[\text{Ni}(\text{NH}_3)_6]^{2+}$, 10,700 cm.^{-1} . For the two divalent complexes, the results for $F = 2.00$ are quite close to those observed experimentally for both choices of the ammonia diagonal element. For the cobalt(III) complex, all of the results are too small, and for the chromium complex, the result using $F = 1.82$ and the NH_3 ionization potential agrees with experiment and the three remaining results are all considerably higher. It would appear from these results that it would probably be possible to get agreement with the experimental values using either choice for the ammonia diagonal element. Since this is true, further work should, perhaps, be carried out

(20) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, Chapter 10.

TABLE IV
 EFFECT OF VARYING F

Complex	F	q	Δ , cm. ⁻¹
[Cr(NH ₃) ₆] ³⁺	1.82	0.506	20,550
	2.00	0.449	24,050
	2.10	0.417	27,400
	2.20	0.388	29,460
	2.30	0.360	31,490
[Co(NH ₃) ₆] ³⁺	1.82	0.486	14,520
	2.00	0.442	16,920
	2.10	0.417	18,200
	2.20	0.393	19,530
	2.30	0.371	20,740
[Co(NH ₃) ₆] ²⁺	1.82	0.366	9,720
	2.00	0.320	11,060
	2.10	0.297	11,840
	2.20	0.275	12,640
	2.30	0.257	13,440
[Ni(NH ₃) ₆] ²⁺	1.82	0.257	8,580
	2.00	0.211	9,750
	2.10	0.187	10,400
	2.20	0.163	11,090
	2.30	0.140	11,840

using the ammonia IP, both for the reasons outlined above from a conceptual standpoint and because it appears that a smaller variation of F will be necessary to achieve correct results for all complexes.

Finally, we turn to the effect of varying F . In these calculations, all factors except F have been held constant. The ammonia diagonal element was taken to be the ionization potential of the ammonia molecule, with the charge dependence of $-84,000$ cm.⁻¹ decided on above. The results are presented in Table IV.

One conclusion is immediately obvious, indeed it was obvious in some of the calculations of Tables II and III. The implicit assumption that a single F will suffice for all calculations, even for a single type of overlap, is simply not true. To obtain correct, or even approximately correct, results it has been neces-

sary to go from $F = 1.82$ for the [Cr(NH₃)₆]³⁺ to $F = 2.30$ for [Co(NH₃)₆]³⁺, and the latter value is still somewhat small. It is apparently not even possible to use a single F to obtain correct results for one metal, as $F = 2.00$ gives the best agreement with experiment for the cobalt(II) complex, whereas $F = 2.30$ or a slightly larger value is necessary to give approximate agreement for the cobalt(III) complex. For the nickel complex, either $F = 2.10$ or $F = 2.20$ gives agreement to within 300 cm.⁻¹ with the experimental value.

A trend is obvious in these results. The F necessary to achieve correct results increases as one passes through the first transition series. This trend is just the opposite of that found for the overlap integrals involving the 3d orbitals and suggests that in fact the magnitude of the off-diagonal elements may remain fairly constant across the series. It is interesting that this effect is precisely that found to be so very useful in the simple Hückel MO treatments of π -electron systems in conjugated organic molecules.

A comparison of the results for the cobalt(II) and cobalt(III) systems is of interest in still another connection. For a given F , the MWH method does predict a considerably smaller Δ for the cobalt(II) complex than for the cobalt(III) complex, in agreement with the observed fact that trivalent Δ are always considerably larger than divalent Δ . On the other hand, the magnitude of the difference is too small, Δ for the divalent complex being about two-thirds that for the trivalent compound, whereas it is observed to be approximately one-half. Thus, although the qualitative prediction is correct, the quantitative result leaves something to be desired. This can, of course, be overcome by the use of different values of F , as shown.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA, AND MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

Cyclohexylaminebis(pentane-2,4-diono)cobalt(II): Existence of Monomer and Dimer

By J. A. BERTRAND, F. A. COTTON, AND W. J. HART¹

Received December 31, 1963

Methods of preparing the 1:1 adduct of bis(pentane-2,4-diono)cobalt(II) and cyclohexylamine are reported. Molecular weight data indicate the presence of a dimer in carbon tetrachloride and a monomer in chloroform; molecular weight and spectral data for benzene solutions of the compound are shown to be consistent with a monomer-dimer equilibrium.

Introduction

Various complexes of bis(pentane-2,4-diono)metal(II) compounds (hereafter abbreviated MA₂) with amines have been reported in the literature. Many diamine complexes have been isolated as solids and are analogous to the common diaquo complexes. Re-

cently, Fackler obtained evidence for pyridine (abbreviated py in formulas) complexes of the formula (MA₂)₂py from spectrophotometric studies on solutions, using either cobalt(II)² or nickel(II)³ as metal ion. He was also able to isolate the solid compounds, but did not report any data other than analyses for the solids. In addition, Fackler found evidence for a

(1) N.S.F. Faculty Research Participant, Georgia Institute of Technology, 1963.

(2) J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963).

(3) J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962).