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DIFFERENCES BETWEEN THE FOUR HALIDE LIGANDS, AND DISCUSSION REMARKS ON TRIGONAL-BIPYRAMIDAL COMPLEXES, ON OXIDATION STATES, AND ON DIAGONAL ELEMENTS OF ONE-ELECTRON ENERGY

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1. DIFFERENCES BETWEEN THE FOUR HALIDE LIGANDS

The comparison between a series of smoothly but widely varying ligands is one of the main objectives of chemistry. There is no doubt that the four halides represent one of the most favourable cases for theoretical study. We shall try here to summarize the various properties known for this series.

It is now well established that the electron affinity of F, Cl, Br and I atoms (or in other words, the ionization energy of gaseous F^-, . . .) is nearly invariant, contrary to previous belief, in the interval 25–29 *kK* ($1\ kK = 1000\ cm^{-1} = 0.124$ eV = 2.85 kcal/mole). On the other hand, the ionization energies of the neutral atoms are, in *kK*: F 140.5, Cl 105.0, Br 95.6 and I 84.3. Hence, Mulliken's proposal of defining the electronegativity x as the average values of these two quantities produces the slope $dE/dx = 20\ kK$ if Pauling's scale is employed. It is possible[1] to define optical electronegativities x_{opt} from the striking regularities in the electron transfer spectra caused by transitions of an electron from the filled M.O. mainly situated on the ligands to the partly filled *d* shell concentrated on the central transition group atom:

F 3.9 Cl 3.0 Br 2.8 I 2.5

However, in this case, dE/dx is 30 *kK*. We return below to the question of the connection with quantum-mechanical calculations.

The electric polarizabilities increase strongly:

F^{-I}	1.0	Cl^{-I}	3.0	B^{-I}	4.2	I^{-I}	6.3	
Ne	0.4	Ar	1.6	Kr	2.5	Xe	4.0	$\times 10^{-24}\ cm^3$

Fajans[2] attempted to derive values for the gaseous ions. Sometimes, the extrapolation from the isoelectronic noble gases is difficult. Thus, O^{2-} looses an electron spontaneously and has an infinitely high polarizability, whereas O^{-II} in BaO has 2.1, in CaO 1.9, MgO 1.7, Al_2O_3 1.35, SO_4^{2-} 1.2 and in ClO_4^- only 1.1

A symposium[3] was held at CERI in May 1965 to consider Pearson's soft and hard Lewis acids and bases[4]. It was concluded that there is a definite relation between the first-order (weak field) electric polarizabilities and the concept of softness, but that other effects disturb this simple picture. Thus, Cs^{I} has a higher polarizability, 3.0, than 2.4 for Ag^{I}, contrary to all chemical evidence. However, intuitively, one of the most typical properties of the halogens is the hardness of fluoride and softness of iodide.

A great number of papers have recently appeared concerning the application of the Wolfsberg-Helmholz model to transition group complexes[5]. Closely related to the Hückel model, the non-diagonal elements of energy are, under equal circumstances, proportional to the overlap integral between the central atom and ligand orbitals of definite symmetry type. If we are interested in the relative behaviour of the five *d* or seven *f* orbitals, the corollary the "angular overlap model" (which can be shown to be equi-consequential with a contact term at each ligand nucleus) is highly illustrative[6–8].

However, the diagonal elements of such models pose nearly epistemological questions. The four halides are unique in forming monatomic anions, in certain compounds such as CsCl or CaF_2, which are very close to pure electrovalent bonding. Conventional Wolfsberg-Helmholz treatment suggests considerable covalent character of such salts. This discrepancy can be removed if the strong influence of Madelung-like terms due to adjacent charged atoms is considered[1,9]. Actually, it is possible to differentiate the Madelung energy with respect to the fractional atomic charge z and account for the situation suggested by the optical electronegativities that the ionization energy of a given halide is nearly invariant with z and comparable to the ionization energy of the neutral halogen atom.

Another reason to believe that

$$(5+30\,x_{\mathrm{opt}})\ kK$$

is a fair approximation to the actual ionization energy of the highest filled M.O. comes from studies of gaseous molecules. Unfortunately, the differences between x_{opt} for central atoms (say Ru^{III} 2.1, Ru^{IV} 2.4, Rh^{IV} 2.6) and for ligands do not correspond directly to differences of M.O. energies because of charge separation effects[1] which correspond mainly to the difference between the two Coulomb integrals $J(d, d)-J(\pi, d)$. Hence, the 3*d* shell ionization energy may be some 20 to 40 *kK* larger than expected from the value of x_{opt}, and sometimes larger than the ionization energy of the filled π orbitals of the ligands.

One may attempt more direct ways of finding the charge distribution in the compounds and minimizing the total energy. An approximate solution involves the differential ionization energy including the differential quotient of the Madelung energy[1,10] as discussed in section 4. The nephelauxetic effect[11,12] increases strongly from F^- to I^- and is excellent experimental evidence for increasing delocalization and expansion of the partly filled shell when the difference $x_{\mathrm{opt}}(X)-x_{\mathrm{opt}}(M)$

decreases. It is worth noting that the central atoms in most cases behave as if the fractional charge is well above 1 though it is always below the oxidation number. This deviation from Pauling's electroneutrality principle can be explained again by the Madelung interactions.

From the chemist's point of view it would be satisfactory to predict the relative stability of central atom oxidation states. Stereochemical requirements are complicated[13,14] and may explain the occurrence of OsO_4 (though only OsF_6, $OsOF_5$) and MnO_4^- (but not MnF_7). The softness of low and of very high[15] oxidation numbers of central atoms may either be connected with a non-monotonic variation of the fractional central atom charge or with low-lying energy levels caused by adjacent empty and filled orbitals. There must be a lower limit of permissible values of $x_{opt}(X)-x_{opt}(M)$ as a necessary condition for a halide not to decompose, forming free halogen molecules, but this limit depends on the variation of the potential surfaces as function of the internuclear distances.

Recently all the mixed iridium(IV)chloro/bromo complexes have been separated by electrophoresis[16]. Such mixed, robust complexes are thermodynamically somewhat more stable than expected from statistical considerations.

The Chairman of the conference on "Mechanistic and structural aspects in the chemistry of metal complexes", Professor Turco, was so kind as to permit me to submit for publication in the proceedings of the conference various remarks from the lively discussion rather than an extension of the essay on halides. There are various reasons; partly because the extension would seem tedious and artificial, and partly because reviews on the chemical bonding in halogen compounds[17] and on soft and hard Lewis acids and bases[18] are under preparation.

2. TRIGONAL-BIPYRAMIDAL COMPLEXES

At this conference, Ciampolini reported absorption spectra of five coordinate 3*d* group complexes containing the ligand tris(dimethylaminoethyl)amine $N(CH_2CH_2N(CH_3)_2)_3$ with four tertiary nitrogen atoms, whilst Sacconi reported Schiff base complexes, known from X-ray crystallography to contain dinuclear chromophores $N_2OM^{II}O_2M^{II}N_2O$ consisting approximately of two trigonal-bipyramidal chromophores $M^{II}N_2O_3$ (the two N and one bridging O atom in the equatorial plane) joined together.

In both cases, the authors proposed to interpret the absorption spectra by ligand field theory, assuming to a first approximation a trigonal-bipyramidal chromophore MX_5 of symmetry D_{3h}. The fairly complicated energy levels predicted seem to be in good agreement with the band maxima observed. In my opinion, it is worthwhile to analyze these results more closely, because they can be based on more general properties of a group-theoretical nature and on the angular overlap model, whereas the results reported at the conference were obtained by the point dipole electrostatic model which is highly unsatisfactory in many other contexts[19].

The angular overlap model originally took only σ-anti-bonding effects into account[6] but was later extended to π- and higher λ-values[7]. The contributions to the d-orbital energies in trigonal-bipyramidal MX_5 with five identical M–X distances are

$(z^2-\frac{1}{3}r^2)$	$\sigma(a_1')$	$\frac{11}{4}e_\sigma$
xz, yz	$\pi(e'')$	$\frac{7}{2}e_\pi$
$xy, (x^2-y^2)$	$\delta(e')$	$\frac{9}{8}e_\sigma+\frac{3}{2}e_\pi$

where the z-axis goes through the two perpendicular ligands. If only p or d^3 orbitals are considered (and not f orbitals[6]) the trigonal symmetry D_{3h} has exactly the same consequencies as the linear symmetry $D_{\infty h}$. Consequently, we simplify the following discussion by using the notation of λ-orbitals and (Λ, S)-terms appropriate for linear symmetry, somewhat in analogy to the quantum number μ defined by Hellwege[20]. One of the main advantages of the angular overlap model is that the parameters e_σ and e_π are transferable from one chromophore MX_q to another MX_p of different symmetry if all M–X distances are the same. Thus, the sub-shell energy difference Δ in octahedral chromophores MX_6 is represented by $3e_\sigma-4e_\pi$, roughly 30 percent more than the energy difference between the extreme orbital energies $\sigma(a_1')$ and $\pi(e'')$ in MX_5. However, if the M–X distances are somewhat shorter in MX_5 than in MX_6, e_σ is expected to be somewhat larger in the former case.

The well-defined orbital configurations (corresponding with the strong-field diagonal elements) consist of the following terms for two electrons:

σ^2	$^1\Sigma$			
$\sigma\delta$	$^3\Delta$,	$^1\Delta$		
$\sigma\pi$	$^3\Pi$,	$^1\Pi$		
δ^2	$^3\Sigma$,	$^1\Sigma$,	$^1\Gamma$	
$\delta\pi$	$^3\Phi$,	$^3\Pi$,	$^1\Phi$,	$^1\Pi$
π^2	$^3\Sigma$,	$^1\Sigma$,	$^1\Delta$	

For eight electrons, the same relative order of energy levels is obtained according to Pauli's hole-equivalence theorem, except that the apparent one-electron energies, now representing holes, are inverted. Hence, the groundstate of a low-spin d^8 complex is $^1\Sigma$ tending towards the configuration $\pi^4\delta^4$ which lacks the two electrons σ^2.

However, in our special case, partly because the complexes reported by Ciampolini and Sacconi are high-spin, it is more profitable to consider the weak-field diagonal elements. The squares of the amplitudes of the strong-field functions and the corresponding energies are:

${}^3\Phi({}^3F)$: $\delta\pi$	$E(\pi)+E(\delta)$
${}^3\Delta({}^3F)$: $\sigma\delta$	$E(\delta)+E(\sigma)$
${}^3\Pi({}^3F)$: $\frac{3}{5}[\delta\pi]+\frac{2}{5}[\sigma\pi]$	$E(\pi)+\frac{3}{5}E(\delta)+\frac{2}{5}E(\sigma)$
${}^3\Sigma({}^3F)$: $\frac{4}{5}[\pi^2]+\frac{1}{5}[\delta^2]$	$\frac{8}{5}E(\pi)+\frac{2}{5}E(\delta)$
${}^3\Pi({}^3P)$: $\frac{3}{5}[\sigma\pi]+\frac{2}{5}[\delta\pi]$	$E(\pi)+\frac{2}{5}E(\delta)+\frac{3}{5}E(\sigma)+15B$
${}^3\Sigma({}^3P)$: $\frac{4}{5}[\delta^2]+\frac{1}{5}[\pi^2]$	$\frac{2}{5}E(\pi)+\frac{8}{5}E(\delta)+15B$

as can most easily be seen from the condition of occupation in the ratio $2\delta:2\pi:\sigma$ in each term ${}^3P$ and ${}^3F$.

Since the secular determinants of ${}^3\Pi$ and ${}^3\Sigma$ are only of second degree, it is very easy to evaluate the non-diagonal elements according to eqn. (93) of ref. 19 (this was done in half an hour one evening in Bressanone), their numerical values are

$$\frac{\sqrt{6}}{5}\{E(\sigma)-E(\delta)\} \qquad \text{for } {}^3\Pi$$

and

$$\frac{4}{5}\{E(\delta)-E(\pi)\} \qquad \text{for } {}^3\Sigma$$

It is possible to use the Pauli and Van Vleck operators[21] to show that the relative energy of the levels of maximum spin for $S = 3/2$ of d^7 is exactly the same as for $S = 1$ of d^2, and that all the apparent one-electron energies (but not B) are inverted for $S = 1$ of d^8 and $S = 3/2$ of d^3.

Assuming a reasonable value of the nephelauxetic effect, B can be estimated to be 800 cm^{-1} in Ciampolini's cobalt(II) and nickel(II) complexes. Since the sub-shell energy difference Δ is 10900 cm^{-1} in octahedral[22] $\text{Nitren}(H_2O)_2{}^{2+}$ we expect the energy difference $E(\sigma)$–$E(\pi)$ to be some $12B$ with the arguments given above. If we actually assume $E(\sigma)$–$E(\delta) = 8B$ and $E(\delta)-E(\pi) = 4B$, the energy levels are, relative to the groundstate as zeropoint:

d^8:		d^7:	
${}^3\Delta$	0	${}^4\Sigma$	0
${}^3\Pi$	$7.7B$	${}^4\Phi$	$2.9B$
${}^3\Phi$	$12.0B$	${}^4\Pi$	$5.2B$
${}^3\Sigma$	$13.5B$	${}^4\Delta$	$14.9B$
${}^3\Pi$	$23.3B$	${}^4\Sigma$	$20.8B$
${}^3\Sigma$	$25.5B$	${}^4\Pi$	$23.6B$

in satisfactory agreement with Ciampolini's spectra though $B \sim 700$ cm^{-1}, $E(\sigma)-E(\delta) = 10B$ and $E(\delta)-E(\pi) = 5B$ might give slightly better agreements. One of Professor Sacconi's slides showed the actual one-electron energies assumed for d^9, the difference $E(\sigma)-E(\delta)$ being considerably more positive than $E(\delta)-E(\pi)$. Again using the Van Vleck operator, one readily sees that high-spin d^6 systems as represented by Fe^{II} complexes have the same quintet levels as the doublet of d^1, agreeing with observations.

An interesting aspect of these absorption spectra is the relatively low intensity of the bands; the molar extinction coefficients ε are above 100 only for the two last bands which are predominantly F–P transitions (generally having the highest ε in typical weak-field complexes). Venanzi[23] and collaborators studied a large number of five-coordinate, usually low-spin, complexes (of quadridentate phosphines and arsines) which frequently have very strong bands in the visible. In the light of the results for the hexamethyl-tren complexes, one suspects that the bands with $\varepsilon \sim 5000$ cannot be due to internal d shell transitions but are electron transfer bands. This conclusion is also important for the band at 18000 cm^{-1} of the recently reported[24] trigonal-bipyramidal low-spin ($S = 1$) $CoCl_3(P(C_2H_5)_3)_2$. Since a similar band is observed at 17000 cm^{-1} in the analogous $CoBr_3(P(C_2H_5)_3)_2$, it is due to electron transfer, not from orbitals mainly localized on the halide ligands, but from the phosphine σ-bonding lone-pairs. The simultaneous existence of low-spin (d^6 $S = 1$; d^8 $S = 0$) phosphine and arsine complexes and of high-spin tertiary amine complexes suggest a rather dramatic variation of the ratio between the orbital energy differences and interelectronic repulsion parameters such as B. The nephelauxetic decrease of B in phosphine and arsine complexes may be an important factor in this development.

It cannot be entirely excluded that the band intensities are some 50 times larger in low-spin arsines than in high-spin ammines, but it does not seem very plausible. Dyer, Hartley and Venanzi[25,26] found a small variation in the wavenumber of the first absorption band of $NiXqas^+$, $PdXqas^+$ and $PtXqas^+$ as function of X, following the spectrochemical series. However, this would also be true for an electron transfer band caused by the transition from a filled orbital of nearly constant optical electronegativity x_{opt} to the σ-anti-bonding orbital $\sigma(a_1')$. If the non-bonding orbitals (here $\pi(e'')$ neglecting π-anti-bonding effects) of all the nickel(II) complexes[27] have $x_{opt} = 2.1$, and we estimate $x_{opt} = 1.6$ for the empty $\sigma(a_1')$ in low-spin $NiXqas^+$, then with the spin-pairing energy (for $S = 0 \rightarrow \frac{1}{2}$) being $\frac{4}{3}D \sim 3000$ cm^{-1} (= 0.1 electronegativity unit), and the first absorption band appearing at 15000–18000 cm^{-1}, this would make $x_{opt} = 2.2-2.3$ for the quadridentate arsine ligand.

This rather bold hypothesis may be checked by comparison with the spectra[28] of *trans* and *cis*-$Codas_2Cl_2{}^+$ and $Codas_2Br_2{}^+$. If we assume $x_{opt} = 2.4$ for the lower sub-shell and 1.6 for the higher sub-shell, and a wavenumber decrease due to spin-pairing energy corresponding with 0.1 unit, then the electron transfer band at 25000 cm^{-1} in the former species suggests $x_{opt} = 2.5$ for the diarsine ligand. This would cast considerable doubt on the identification of the first absorption band of $NiXqas^+$ as an electron transfer band if it were not for the fact that the next strong absorption band of $NiXqas^+$ occurs 15000 cm^{-1} higher (which would move x_{opt} for qas at least up to 2.7). Another argument supporting a value for $x_{opt} = 2.2$ for qas is the fact that $PdIqas^+$ has a band[26] at 26000 cm^{-1} which does not seem to occur in $PdBrqas^+$ and $PdClqas^+$, and we know that I^- has $x_{opt} = 2.5$.

After all, it is not inconceivable that the presence of nine benzene rings in qas and only one benzene ring in das suffices to make the former ligand considerably more reducing. This would be in agreement with the chemical fact[13] that Ru das_2X_2 is fairly readily oxidized to strongly coloured Ru $das_2X_2^+$ whereas Ru $qasX_2$ has only been oxidized[29] briefly to Ru^{III}.

A crucial test would be the observation that in low-spin $FeXqas^+$ or $CoXqas^+$, if they exist, the transitions $\pi(e'') \rightarrow \delta(e')$ (expected in the infrared) and $\delta(e') \rightarrow \sigma(a_1')$ have moderate intensity.

The fundamental difference between chromophores having a centre of inversion (such as octahedral MX_6 or quadratic MX_4) and those distinctly lacking such a centre is perhaps that in the former case, the intermixing of internal transitions in the partly filled shell and of electron-transfer transitions is only caused by vibronic interactions having apparent non-diagonal elements[19] of the same order of magnitude, 1500 cm^{-1}, as the band half-widths, whereas in the latter case, if the two types of transitions are separated by some 10000 cm^{-1}, there may still be 10 to 40% electron-transfer character of the first absorption band, the non-diagonal element now being due to the one-electron operator.

Coming back to ligand field theory and the similarity between D_{3h} and $D_{\infty h}$ seen from the point of view of *d* orbitals, analogous remarks have been made, by Robertson and McConnell[30], about the similarity of D_{5h} (in cyclopentadienides) and $D_{\infty h}$. Linear XMX has been discussed[31] but it would appear[32] that diatomic molecules MX formed by transition group atoms usually contain one *s*-like electron screening the partly filled *d* shell.

The relativistic effects would be expected to broaden the transition from $^3\Delta$ to $^3\Phi$ of trigonal-bipyramidal high-spin nickel(II) complexes because the width of $^3\Phi$ is $3\varsigma_{3d} \sim 1800\ cm^{-1}$.

3. THE DEFINITION OF OXIDATION STATES

For the chemist, one of the most valuable results of ligand field theory is perhaps a better understanding of oxidation states. This concept can be based on spectroscopic and magnetic studies but does not involve the hypothesis of nearly exclusive electrovalent bonding which would be valid only in a very restricted class of compounds, such as the alkali metal halides and a few other cases like CaF_2. The absorption spectra of complexes such as $Cr(NH_3)_6^{3+}$, MnF_6^{2-}, $Co(S_2P(OC_2H_5)_2)_3$ and $RhCl_6^{3-}$ most clearly indicate the presence of the chromophores $Cr^{III}N_6$, $Mn^{IV}F_6$, $Co^{III}S_6$ and $Rh^{III}Cl_6$ though nobody today would defend the assumption that the success of the ligand field description is based on the central ion charges being close to Cr^{3+}, Mn^{4+}, Co^{3+} and Rh^{3+}. Actually, it is possible to estimate the decrease in the central atom charge to a fractional value, frequently between +1 and +2, from the absorption spectra by studying the nephelauxetic effect[12], *i.e.* the decrease of the parameters of interelectronic repulsion below the values observed for the corresponding gaseous ion M^{z+}.

There is no inherent contradiction between the occurrence of fractional atomic charges (which cannot be defined too sharply) and integral oxidation states. It is at the same time true that the preponderant configuration Ψ_0 or the preponderant atomic orbital ψ_0 in a series expansion of the type

$$\Psi = 0.9\ \Psi_0 + 0.2\ \Psi_1 + 0.1\ \Psi_2 + \ldots\ldots$$
$$\psi = 0.9\ \psi_0 + 0.4\ \psi_1 + 0.1\ \psi_2 + \ldots\ldots$$

does not have the coefficient one, yet it is nevertheless the major constituent. In particular, *if* the coefficient is larger than 0.71, the square-root of a half, no other contribution can be as large. However, in my opinion, the fundamental properties of preponderant configurations are not connected with this, purely numerical, question but rather with the surprising fact that, usually, the symmetry types of the groundstate and the lowest excited levels correspond to those predicted by the preponderant configuration and its appropriate one-electron substitutions. I believe that one may apply Bertrand Russell's theory of types (*cf.* a recent discussion of categorical propositions[33]) and say that the preponderant configurations are properties of higher type of the manifold of all the low-lying states.

Anyhow, the only reasonable definition (so far as I can see) of oxidation states is connected with preponderant configurations. If the groundstate of the chromophore MX_N has a preponderant configuration of molecular orbitals ψ each having a preponderant component ψ_0 either on M or the atoms X, the oxidation state of M can *frequently* be estimated by comparison with the preponderant configuration (involving *nl*-orbitals) of the corresponding gaseous ion M^{z+}. For instance, manganese complexes

Mn^{VII}	Mn^{VI}	Mn^{V}	Mn^{IV}	Mn^{III}	Mn^{II}	Mn^{I}
$3d^0$	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$

have well-defined oxidation states if their preponderant configurations contain partly filled shells occupied by 0,1,2,...electrons. It is no requirement that the partly filled shell should be exclusively localized on the manganese central atom; however, it should have a predominant component ψ_0 of 3*d*-like character (though probably with expanded radial function relative to the gaseous ion).

The famous observation by Owen and Stevens[34] of nuclear hyperfine-structure in the electron spin resonance curves of $IrCl_6^{2-}$ and $IrBr_6^{2-}$ does not affect the description as Ir^{IV}. The hexachloro complex contains a partly filled sub-shell accommodating five electrons (and at most six would be possible, as in Ir^{III}). The squared amplitudes in the L.C.A.O. approximation are 0.76 close to the iridium nucleus and 0.04 close to each of the six chlorine nuclei. It would not be expected that L.C.A.O. is so good an approximation in all cases that the sum of the squared coefficients close to each nucleus is normalized exactly to one. However, there is no doubt that the preponderant component ψ_0 is centered on the iridium atom in our case. Suppose that Owen and Stevens' experiment had given the result that 28% of the uncompensated spin density (of the "hole") were localized on Ir and 12% on each of the six Cl, one would have had a *collectively oxidized* set of ligands Cl_6^{5-} and the oxidation state of the central atom would have been Ir^{III}. This follows because the $5d$ sub-shell would have been the preponderant component of three filled π-bonding orbitals of lower energy. Suppose finally that a closed-shell system without the five $5d$-like electrons such as $HfCl_6^{2-}$ had been considered. This is, according to our definitions, the Hf^{IV} complex of the normal set of ligands Cl_6^{6-}. However, if the three degenerate (because of the octahedral symmetry) highest filled orbitals had their preponderant component ψ_0 on Hf rather than on Cl, we would classify the entity as Hf^{-II} and six Cl^0. It is worth remarking that closed-shell systems have oxidation states which jump many units, if there is any change; it is possible to show that colourless tetrachlorides with no low-lying excited levels such as CCl_4 or $SiCl_4$ could only be $M^{IV}Cl^{-I}$ or $M^{-IV}Cl^{I}$ according to our definitions[35]. There is a close connection between the well-defined behaviour of the colourless $HfCl_6^{2-}$ and the low-lying electron transfer bands of strongly coloured $IrCl_6^{2-}$ approaching a situation switching over to Ir^{III} and Cl_6^{5-}.

Ligands are innocent[3,18] when they allow oxidation states of the central atoms to be defined. The simplest case of a suspect ligand is NO. In octahedral complexes of the type $M(CN)_5(NO)^{q-}$ it has been suggested[14,36] that M has the oxidation state $(4-q)$ *if* at most six electrons are present in the lower sub-shell (*i.e.* the lower limit of oxidation states being Cr^0, Mn^I, Fe^{II} and Co^{III}) and the ligands are CN^- and NO^+ isoelectronic with CO and N_2. If the subsequent electrons flow into the two π-anti-bonding orbitals of NO rather than into the σ-anti-bonding orbitals of the central atom, one would obtain d^6-systems of NO, NO^-, NO^{2-} and NO^{3-} rather than d^7, d^8, d^9 and d^{10}. In the case of NO and NO^-, one would expect a tendency (already discussed in another connection by Orgel[37]) to deviate from linear bonding MNO and form more or less irregular triangles, as seem to occur in $CoNO(S_2CN(CH_3)_2)_2$. However, the situation in the NO-complexes is far from clarified and we may have many more surprises. Dr. Gans discussed the infrared spectra of some nitrosyls at this conference; there is no doubt that the invading electron density in NO^+ may make this ligand similar to NO or even approaching NO^- with respect to its stretching force constant, and at the same time, the preponderant configuration may depend on the order of the filled orbitals characterizing NO^+.

The dithio-ligands L discussed at this conference by Harry Gray are another, most interesting category. If we put the z-axis perpendicular to the plane of the four sulphur atoms, and the y-axis bisecting the C–C bonds (*i.e.* the x-axis separating the two ligands) in square planar ML_2^{q-}, it is generally agreed that the highest d-like orbital is the highly σ-anti-bonding xy having the symmetry type b_{1g} in D_{2h} (and corresponding with x^2-y^2 in D_{4h} with the usual coordinate system directed through the ligand atoms in square planar MX_4). This orbital is empty in typical low-spin d^8 systems such as Ni^{II}, Cu^{III}, Pd^{II}, Pt^{II} and Au^{III} forming ML_2^{2-} and ML_2^- with dianion ligands L^{2-}. The orbital (xy) is half-filled in CuL_2^- and AuL_2^- which presumably are Cu^{II} and Au^{II} complexes though, as we saw above, if the preponderant component ψ_0 should be considerably less than 50%, on the central atom, we would then have to consider them as Cu^I and Au^I complexes if the corresponding filled σ-bonding orbital were localized to a greater extent on the central atom. Of course, we might be willing to admit that the expected order of orbitals with correct *symmetry types* still occurred in the preponderant configuration of such a complex and be willing to accept the classification Cu^{II} though perhaps 38% only of the uncompensated spin density would be found on the copper atom. On the other hand, if the symmetry type had not been the same as $b_{1g}(xy)$, this argument would necessitate collective oxidation of L_2^{4-} to L_2^{3-}.

According to paramagnetic resonance results, the half-filled orbital in CoL_2^{2-} ($S = \frac{1}{2}$) has the symmetry type $b_{3g}(yz)$ which hence should be the next-highest, strongly π-anti-bonding, d-like orbital, whereas RhL_2^{2-} probably[38] has $a_g(z^2-\frac{1}{3}r^2)$ if it is not the a_u orbital discussed below. In the former case, Rh^{II} forms a complex with the two dianions L_2^{4-}, in the latter case Rh^I with the collectively oxidized L_2^{3-}.

Gray and collaborators[39] attempted Wolfsberg-Helmholz calculations on various ML_2^{2-} and ML_2^- compounds. It appears that NiL_2^- has some 29% of the uncompensated spin (of a_g symmetry, assumed to be (x^2-y^2)) on Ni and the rest on π-orbitals in the SCCS plane. Though this calculation cannot be considered conclusive evidence, it would suggest a Ni^{II} complex of L_2^{3-} though it might be argued that the π-orbitals perpendicular to the SCCS plane (called π_v by the Columbia group) are more suitable candidates for collective oxidation of L_2^{4-}. Actually, the six (of the eight possible) linear combinations of π_v orbitals expected to be filled have the following nodal-planes besides the xy-plane common to all π_v orbitals:

$1b_{1u}$: none
$1b_{3g}$: xz between the ligands
$2b_{1u}$: two; between all C–S pairs
$2b_{3g}$: three; xz and between all C–S pairs
$1b_{2g}$: yz bisecting the C–C bonds
$1a_u$: xz and yz.

Of these orbitals, $1b_{3g}$ and $2b_{3g}$ form π-bonds with (yz) of the central atom and $1b_{2g}$ with (xz) of the central atom. The loosest bound orbital, $1a_u$, has three orthogonal nodal-planes like the f-orbital xyz and is not expected to induce any bonding with the central atom. Hence, it might be proposed that collectively oxidized L_2^{3-} (which may occur in certain ML_2^-) contains only one rather than two $1a_u$ electrons in the preponderant configuration, and that NiL_2 is a Ni^{II} complex of the set L_2^{2-} having an empty $1a_u$ orbital. Thioketones 2L would lack both $1b_{2g}$ and $1a_u$ electrons, or perhaps $2b_{1u}$ and $2b_{3g}$.

The existence of species[40] such as VL_3 clearly shows that L does not always behave as a dianion. The vanadium hyperfine structure is so strong that the unpaired electron is mainly on the central atom; I suspect the presence of vanadium(IV) and L_3^{4-} of the form discussed below, but it cannot be excluded *a priori* that V^{II} and L_3^{2-} may occur. The magnetic resonance evidence is less clear-cut[40,41] for species such as VL_3^{2-}, CrL_3^-, MoL_3^- and WL_3^- which might, as an extreme, be V^{IV} and Cr^{V} complexes of L_3^{6-} with very low-lying electron transfer levels.

Harry Gray has presented evidence at this conference that ReL_3, and indeed most ML_3, ML_3^- and ML_3^{2-} compounds have the trigonal prismatic structure D_{3h} rather than antiprism D_{3d} derived from a slightly distorted octahedron. The angular overlap model, taking only σ-anti-bonding into account[6], suggests $\sigma(z^2 - \frac{1}{3}r^2)$ at lowest energy in prismatic shapes in which the parameter ξ does not differ much from $\sqrt{3/7}$ as indicated by Gray (the square sides of the prism having $\sqrt{3}\xi = 2\zeta$) followed by $\delta(x^2 - y^2$ and $xy)$ and, at much higher energy, $\pi(xz, yz)$. Actually, the σ-antibonding energy is $\frac{6}{49}e_\sigma$, $\frac{36}{49}e_\sigma$, and $\frac{108}{49}e_\sigma$ in this particular case. Hence, the one-electron energies are not very different from those in an octahedral MX_6, but the more-electron levels can be rather different. Thus, if CoL_3^{3-} $(S = 0)$ was a low-spin trigonal-prismatic complex, the groundstate would be $^1\Sigma$ from $\sigma^2\delta^4$, and the first excited configuration $\sigma^2\delta^3\pi$ would consist of the energy levels $^{3,1}\Phi$, Π in contrast to octahedral CoL_3^{3-}.

The nine π_v orbitals of L_3^{6-} in a prismatic complex are expected to fall in various groups, the highest energy being represented by a rather isolated linear combination of symmetry a_1'' in D_{3h} having four nodal-planes (like a *g* orbital in spherical symmetry), one bisecting all three C–C bonds with three nodal-planes perpendicular to the first plane, producing a hexagon of alternative positive and negative regions in each of the two planes containing three sulphur atoms. Because of the first nodal-plane mentioned, the two hexagons are out of phase and would constitute a system having a centre of inversion if they were regular.

If the collective oxidation of the ligands in prismatic ML_3^{q-} involve the sets L_3^{5-} and L_3^{4-} lacking one or two a_1'' electrons, respectively, and if oxidation states and preponderant configurations can be introduced that way, we are closest to an easily classified behaviour of the conjugated dithio-ligands that we can hope for. The truth may be far more complicated, and further study of absorption spectra would be highly useful. In many ways, the determination of oxidation states is more a problem for the spectroscopists than for the chemists, and it is usually, but not always, possible after sufficient investigation.

4. THE INFLUENCE OF MADELUNG ENERGY ON THE DIAGONAL ELEMENTS OF ONE-ELECTRON ENERGY

The treatment of organic molecules by Hückel's model is remarkably successful in many respects. It is only the last ten years that it has slowly become apparent that typical inorganic compounds can be discussed along similar lines. However, the transition group complexes are usually so definitely heteronuclear that the choice of diagonal elements is a far more difficult problem than in most aromatic molecules. The other problem of the non-diagonal elements is comparable in the two cases and seems to be less ambiguous though the Wolfsberg-Helmholz treatment has not yet found a solid quantum-mechanical foundation[1,10]. A general tendency recently is to assign fractional charges to the central atoms in the interval 0 to 1, as is true for Dr. Oleari's results as well. This feature is in dissonance with much physical evidence, *e.g.* the extent of the nephelauxetic effect[12].

If the isolated atoms and monatomic ions are considered, the total energy T can be written as a fairly short Taylor series[1,42] in the charge z:

$$T = -T_0 + a_0 z + \tfrac{1}{2} a_1 z^2 + \tfrac{1}{3} a_2 z^3 + \ldots$$

the differential quotient of which

$$\mathrm{I}(z) = a_0 + a_1 z + a_2 z^2 + \ldots$$

is called the differential ionization energy and connected to experimental facts by the requirement that the ionization energy $\mathrm{M}^{+q-1} \rightarrow \mathrm{M}^{q+} + e^-$ is

$$\mathrm{I}(\mathrm{q}) = (a_0 - \tfrac{1}{2} a_1 + \tfrac{1}{3} a_2) + (a_1 - a_2)\mathrm{q} + a_2 \mathrm{q}^2$$

One might attempt[1] to minimize the total energy of a polyatomic molecule by equilibrating the differential ionization energy of the individual atoms. In treatments of the Hückel or Wolfsberg-Helmholz type, one finds eigenvalues of secular determinants corresponding to one-electron energies, and the sum of these is less negative than the total energy because the interelectronic repulsion terms have been taken into account twice. However, besides this more technical question, it is quite clear that the Madelung energy

$$-\alpha z^2/(r_\mathrm{M} + r_\mathrm{X})$$

must be included in the total energy. α is a constant characterizing the geometry of the molecule or crystal (many of my colleagues believe that "Coulombic interatomic terms" or similar would be a more appropriate name in the former case) such as 1 for diatomic MX, about 1.75 for crystalline MX, 3.5 for gaseous linear XMX, ~5 for crystalline MX_2, 12.33 for tetrahedral MX_4 and 26.01 for octahedral MX_6. z is the charge of the X-atom and $(r_\mathrm{M} + r_\mathrm{x})$ the internuclear distance M–X.

Let us concentrate our attention on a neutral molecule MX_N (such as $HgBr_2$, VCl_4 or IrF_6). We define an ionicity parameter ξ so that the fractional charge on the central atom is $+N\xi$ and on each ligand atom $-\xi$. The question is now what to do with the Madelung energy $-\alpha\xi^2/(r_\mathrm{M} + r_\mathrm{X})$. One approach is to differentiate it with respect to ξ, and to add it to the expression for the differential ionization energy of M after division by N:

$$I_M(N\xi) = a_{M0}+a_{M1}N\xi+a_{M2}N^2\xi^2-\alpha\xi/N(r_M+r_X)$$

and to divide it with N and subtract it from the differential ionization energy of X:

$$I_XN(\xi) = a_{X0}-a_{X1}\xi+a_{X2}\xi^2+\alpha\xi/N(r_M+r_X)$$

Since a_1 for the four halogens is in *kK* (= 1000 cm^{-1})

F 127 Cl 82 Br 73 I 61

the dependence of I_X on ξ nearly disappears in many cases because $\alpha/N(r_M+r_X)$ in the unit 115 *kK*/Å is roughly 100 *kK*. In octahedral molecules, α/N has the unusually high value 4.34, and the variation of I_X with ξ tends to be inverted. For typical central atoms, a_1 is some 60 to 100 *kK*, and $a_{M1}N\xi$ again tends to be cancelled or overcompensated by the differential Madelung term.

An alternative attitude is to consider the ionization energies at $+N\xi$ and $-\xi$, *i.e.* the expressions

$$I_M = (a_{M0}+\tfrac{1}{2}a_{M1}+\tfrac{1}{3}a_{M2})+(a_{M1}+a_{M2})N\xi+a_{M2}N^2\xi^2$$
$$I_X = (a_{X0}+\tfrac{1}{2}a_{X1}+\tfrac{1}{3}a_{X2})-(a_{X1}+a_{X2})\xi+a_{X2}\xi^2$$

and to add the Madelung potentials $-N\xi/(r_M+r_X)$ to I_M and

$$+\left(\frac{2\alpha}{N}-N\right)\xi/(r_M+r_X)$$

to I_X, again making the difference I_X-I_M positive rather than it would have been otherwise. If ionization energies I_a of excited, empty orbitals a are to be considered, they are defined by the equation

$$I_a = E_a+J(a, a)$$

E_a being the electron affinity of the orbital and $J(a, a)$ being the Coulomb integral approximately equal to a_1 for the orbital considered. If the parameters a_2 are neglected, one obtains a series of linear relations

$$I(z) = a_0+a_1z$$
$$I_a = a_0+\tfrac{1}{2}a_1$$
$$E_a = a_0-\tfrac{1}{2}a_1$$

to which the Madelung contributions may be added as another parameter proportional to z.

Actually, the Madelung corrections are somewhat too large in their absolute expressions given here. The assumptions of spherically symmetric, non-overlapping ions is not entirely satisfactory. Further, in most molecules (with the exception of CO and crystalline GaAs and similar cases) the chemical bonding corresponding with the non-diagonal elements has the strongest effect, if the fractional atomic charges are close to zero. Of the two, the Madelung energy has apparently been exaggerated by the absolute expressions, but it should be possible to obtain sensible values of the one-electron energies and the distribution of fractional atomic charges by including it to a large extent. Recently, Pearson[9] attempted to calculate bond energies from such a model. In 1966, Horner, Hatfield, Tyree and Jørgensen submitted a paper to the new *International Journal of Quantum Chemistry* on this question.

However, it is my final remark that frequently, it is more fruitful to measure a spectrum during one hour and to speculate about it in an armchair for a day, trying to evaluate the orbital energies by induction and comparison with other facts, rather than to spend a month attempting deductive calculations.

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