# Photo-electron and Chemical Differences Between Scandium, Iron, Cobalt and Gallium*

By CHRISTIAN KLIXBÜLL JØRGENSEN

Département de Chimie Physique, Université de Genève, 1211 Geneva 4

Dedicated to Professor G. SCHWARZENBACH on occasion of his 70th birthday (15.3.1974)

*Summary*

It has been believed that a sufficient explanation of the higher affinity of cobalt (III) to ligands having low electronegativity is the "ligand field" stabilization compared with an interpolation between trivalent scandium, iron and gallium. With photoelectron spectrometers, it is possible to measure much higher ionization energies of the $3d$ shell in zinc (II) and gallium (III) than in systems with partly filled shells. The importance of interelectronic repulsion for the quantum-mechanical treatment and the extent of anti-bonding of the upper sub-shell is discussed as well as the change of inner shell ionization energies going from one element to the next. The behaviour of the lanthanides is more regular.

In the time of ALFRED WERNER, it was quite obvious that the chemistry of Fe (III) and Ga (III) is quite different from Co (III). It is true that they all three form hexaqua ions (also occurring in alums) and the octahedral chromophore M (III) $O_6$ exists in tris (oxalate) anions and in tris (acetylacetonates). Further on, $FeF_6^{-3}$ ($S = 5/2$), $CoF_6^{-3}$ [the only well-characterized cobalt (III) complex having $S = 2$] and $GaF_6^{-3}$ ($S = 0$) are similar though their magnetic properties are so different. However, in aqueous solution, Fe (III) and Ga (III) react only indirectly with most ligands in their role as BRØNSTED bases, forming hydroxo complexes (frequently polymeric) whereas Co (III) is known in a large number of amine complexes of which the "luteo" ion $Co(NH_3)_6^{+3}$ and the "purpureo" ions $Co(NH_3)_5X^{+2}$ are the prototypes. Their preparation often involves oxidation of cobalt (II) complexes, and JANNIK BJERRUM demonstrated that thermodynamic equilibrium could be established on active charcoal. On the other hand, colourless $[Fe(NH_3)_6]X_3$ can be made from anhydrous $FeX_3$ and liquid ammonia at low temperature but such salts decompose above $-50\,°C$. Another striking property of "robust" cobalt (III) complexes is the resolution of optically active enantiomers. In the absence of catalysts, they may take years to racemize. A major part of the collection prepared by S. M. JØRGENSEN and now kept at the Technical University north of Copenhagen is in very good state after 80 years.

For historical reasons, scandium was considered as a rare earth for many years, mainly because it occurs in minerals such as thortveitite together with the heaviest lanthanides.

With the advent of "ligand field" theory it was suggested[1,2] that the difference between Co (III) and, on the other side, Fe (III) and Ga (III) is only a difference in degree and not in essence. In the good approximation of a definite number $n$ of electrons in the upper sub-shell consisting of two anti-bonding orbitals and $m$ in the three lower orbitals in the octahedral chromophore, the "ligand field" stabilization is $(0.6n - 0.4m)\ \triangle$ where $\triangle$ is the sub-shell energy difference (called $10Dq$ in early literature) typically varying between 2 and 4 eV (1 eV = 8068 $cm^{-1}$ = 23.05 kcal/mole). This stabilization vanishes for high-spin ($S = 5/2$) iron (III) having an electron in each of the five $d$-like orbitals ($m = 3$, $n = 2$) and for the closed-shell gallium (III) ($m = 6$, $n = 4$) whereas it is $-2.4\ \triangle$ for low-spin ($S = 0$) cobalt (III) ($m = 6$, $n = 0$). However, this expression is counteracted to a certain extent by the increased interelectronic repulsion. To the first approximation[3,4] the premium to pay for having $S = 0$ rather than $S = 2$ is $6D$ (where the spin-pairing energy parameter $D$ has the order of magnitude 0.8 eV in the $3d$ and $4f$ groups and 0.4 eV in the $4d$, $5d$ and $5f$ groups) obtained from the contribution $-DS(S+1)$ to the interelectronic repulsion in the partly filled shell. Hence, octahedral $d^6$ systems are low-spin when $\triangle/D$ is above 3 and high-spin for lower values of this ratio. For comparison, it may be mentioned that $d^3$ systems such as Cr (III) show the "ligand field" stabilization $-1.2\triangle$. The same is true for octahedral ($S = 1$) $d^8$ systems.

The description of the internal transitions in the $d^6$ configuration of low-spin octahedral complexes, not only of Co (III) but also of rhodium (III) and iridium (III)[5,6] and of the nickel (IV) complex[7,8] $NiF_6^{-2}$ is successful and contributed to the opinion that the "ligand field" stabilization also is described precisely. ORGEL[9] and SCHUIT[10] suggested the alternative of counting the anti-bonding electrons, $n$ being zero for $d^3$ and low-spin $d^6$, $n = 2$ for high-spin forms of $d^5$, $d^6$ and $d^8$ and $n = 4$ for $d^{10}$. Nevertheless, it was clear that the "ligand field" stabilization is in better agreement with the observed hydration energies[11,12] and trends of complex formation constants[13–15] for bivalent ions of the $3d$ group than for trivalent ions. One reason why the comparison with values interpolated between Ca (II), Mn (II) and Zn (II) without classical ligand field stabilization is more appropriate than between Sc (III), Fe (III) and Ga (III) may be that the coordination number of the scandium (III) aqua ion[16] is higher than 6. Recently, it was

* Received September 14, 1973.

noted in this journal[17] that a second is the geometric mean value of the shortest time-interval $10^{-17}$ sec of chemical significance, and the time somewhat above $10^{17}$ sec since the Universe went through a singularity of nuclear density. By the same token, the very slow reaction of Co(III) and Rh(III) compared with Al(III) and Ga(III) may be a question of about $10^{20}$ or about $10^{12}$ times a characteristic vibrational time of $10^{-13}$ sec. In the ARRHENIUS equation, these two exponents, 20 and 12, are roughly proportional to the activation energy. Even the largest activation energies known from chromium(III) and cobalt(III) reactions are only slightly above 1 eV representing less than half of $\triangle$. It is possible to apply arguments based on the angular overlap model[4] to explain the variation of the activation energy with the number of *d*-like electrons[18]. In the period 1957 to 1972 it was felt by many chemists that Co(III) is essentially Ga(III) modified by "ligand field" stabilization, the ionic radius decreased by the lack of the four anti-bonding electrons, the complex formation constants increased for ligands (such as ammonia, nitrite and *a fortiori* cyanide) having $\triangle$ larger than water, and the kinetics dramatically slowed down.

Photo-electron spectrometry of gases[19] and solids[20, 21] permit the measurement of the ionization energy $I$ of penultimate M.O. and inner shells. One of the great surprises to the chemist is that certain $3d$ group compounds[22] and the great majority of $4f$ group compounds[23, 24] have $I$ of the partly filled shell *larger* than of the loosest bound, fully occupied M.O. Before we return to the specific behaviour of cobalt(III) in this respect, it is worthwhile to discuss the variation $dI/dZ$ of the inner shells as a function of the atomic number $Z$.

It is quite clear that the properties of *e.g.* the two-electron monatomic systems from helium to $U^{+90}$ are perfectly smooth as a function of $Z$. However, when several $nl$ shells are filled, $I$ is perceptibly influenced by the least bound shell in the process of completion. COSTER[25] pointed out that the lanthanides containing from one to fourteen $4f$ electrons going from cerium(III) to lutetium(III) have unexpected small increases of $I$ of all the inner shells. It can be seen on a plot[26] between $Z = 39$ and 83 that $dI/dZ$ for both $3p$, $3d$ and $4d$ electrons are 12 eV smaller than expected between $Z = 58$ and 71 showing a spectacular jump between lutetium and hafnium. Figure 1 shows a similar plot for $Z$ between 10 and 60. For each element, an average $I'$ value for a series of typical compounds[27] has been used, in most cases having an uncertainty of 1 to 2 eV. The $I'$ values are corrected for the quasi-stationary positive potential induced on the surface of non-conducting samples[27]. When the $p$ and $d$ signals are resolved in two $j$ components, we consider the $p_{3/2}$ and $d_{5/2}$ signals. We find in eV:

$I'(2p)$: Ne 22, Na 36, Mg 54, Al 80, Si 109, P $\sim$ 140, S $\sim$ 170, Cl(− I) 205, Ar 249, K 297, Ca 353, Sc 409, Ti 464, V 522, Cr(III) 583, Mn 648, Fe 714, Co 787, Ni 861, Cu 939, Zn 1027, Ga 1123, Ge 1226, As $\sim$ 1331.

$I'(3p)$: Cl(− I) 12, Ar 16, K 22, Ca 30, Sc 39, Ti 43, V 46, Cr(III) 50, Mn 55, Fe 60, Co 67, Ni 74, Cu 82, Zn 93, Ga 111, Ge 131, As $\sim$ 149, Se $\sim$ 168, Br(− I) 187, Kr 214, Rb 244, Sr 275, Y 307, Zr 339, Nb 371, Mo 403.

$I'(3d)$: Ni 10, Cu 11, Zn 16, Ga 26, Ge 39, As $\sim$ 50, Se $\sim$ 62, Br(− I) 74, Kr 94, Rb 116, Sr 139, Y 164, Zr 188, Nb 213, Mo 238, Tc(?), Ru 286, Rh 315, Pd 344, Ag 373, Cd 411, In 451, Sn 492, Sb 536 Te $\sim$ 580, I(− I) 624, Xe 676, Cs 730, Ba 785, La 841, Ce(III) 889, Pr 939, Nd 986.

$I'(4d)$: Rh 8, Pd 9, Ag 11, Cd 17, In 24, Sn 32, Sb 40, Te 49, I(− I) 55, Xe 68, Cs 81, Ba 95, La 109, Ce(III) 115, Pr 122, Nd 128.

The jumps seen on Fig. 1 are far above the experimental uncertainty and attain 8 to 10 eV for $I'(3p)$ at Zn, $I'(3p)$ and $I'(3d)$ at Br and $I'(3d)$ at Ag. That the jumps occur at the halogens and not at the noble gases is determined by the choice of the halides rather than perchlorates or bromates. For our purposes, the jump at the end of the transition groups is more interesting. From a theoretical point of view, it is important to note that $dI/dZ$ rarely approaches the "hydrogenic" value $Z \cdot 27.2\ \text{eV}/n^2$ except for 1s, and that the variation of $dI/dZ$ is rather extensive, the function by no means being monotonic as seen by the jumps downward at scandium and lanthanum. The first-order perturbation energy of a given orbital from an additional proton in the nucleus is the value of $\langle r^{-1} \rangle$ for the orbital in reciprocal bohr units, multiplied by 1 hartree = 27.2 eV.


[1] L. E. ORGEL, *Introduction to Transition-metal Chemistry*, Methuen, London 1960 (2. Ed. 1966).
[2] C. K. JØRGENSEN, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, Oxford 1962.
[3] C. K. JØRGENSEN, *Oxidation Numbers and Oxidation States*, Springer-Verlag, Berlin 1969.
[4] C. K. JØRGENSEN, *Modern Aspects of Ligand Field Theory*, North-Holland Publishing Co., Amsterdam 1971.
[5] C. K. JØRGENSEN, *Acta Chem. Scand. 10* (1956) 500.
[6] C. K. JØRGENSEN, *Adv. Chem. Physics 5* (1963) 33.
[7] G. C. ALLEN and K. D. WARREN, *Inorg. Chem. 8* (1969) 753.
[8] G. C. ALLEN and K. D. WARREN, *Structure & Bonding 9* (1971) 49.
[9] L. E. ORGEL, *J. Chem. Physics 23* (1955) 1819.
[10] G. C. A. SCHUIT, *Rec. Trav. Chim. Pays-Bas 81* (1962) 19 and 481 and *83* (1964) 5.
[11] W. G. PENNEY, *Trans. Faraday Soc. 36* (1940) 627.
[12] J. D. DUNITZ and L. E. ORGEL, *Adv. Inorg. Radiochem. 2* (1960) 1.
[13] J. BJERRUM and C. K. JØRGENSEN, *Rec. Trav. Chim. Pays-Bas 75* (1956) 658.
[14] C. K. JØRGENSEN, *Acta Chem. Scand. 10* (1956) 887.
[15] P. GEORGE and D. S. MCCLURE, *Progr. Inorg. Chem. 1* (1959) 382.
[16] G. GEIER, *Ber. Bunsenges. 69* (1965) 617.
[17] U. P. WILD, *Chimia 27* (1973) 421.
[18] H. YAMATERA, *Bull. Chem. Soc. Japan 41* (1968) 2817.
[19] D. W. TURNER, C. BAKER, A. D. BAKER and C. R. BRUNDLE, *Molecular Photoelectron Spectroscopy*, Interscience, London 1970.
[20] C. K. JØRGENSEN, *Chimia 25* (1971) 213.
[21] W. BREMSER, *Topics in Current Chemistry 36* (1973) 1.
[22] S. EVANS, A. HAMNETT, A. F. ORCHARD and D. R. LLOYD, *Disc. Faraday Soc. 54* (1973) 227.
[23] G. K. WERTHEIM, A. ROSENCWAIG, R. L. COHEN and H. J. GUGGENHEIM, *Physic. Rev. Letters* 27 (1971) 505.
[24] C. K. JØRGENSEN, *Chimia 27* (1973) 203.
[25] D. COSTER, *Naturwiss. 11* (1923) 567.
[26] C. K. JØRGENSEN, *Structure & Bonding 13* (1973) 199.
[27] C. K. JØRGENSEN and H. BERTHOU, *Mat. Fys. Medd. Dan. Vid. Selskab 38* (1972) No. 15.

When two neutral atoms having the atomic numbers $Z$ and $(Z+1)$ are compared, it is expected that this perturbation energy is diminuished by $\langle r^{-1} \rangle$ hartree for the outer electron added. The latter expression can be above 15 eV in the $3d$ and $4f$ groups but only some 5 eV for alkaline and alkaline-earth atoms. The corresponding discontinuities on Fig. 1 have slightly more complicated

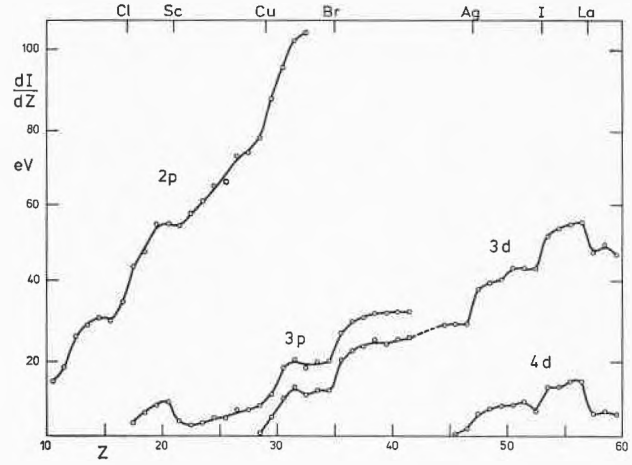


Fig. 1. The variation of ionization energies of $2p$, $3p$, $3d$ and $4d$ shells from one element to the next between neon and neodymium

origins, the MADELUNG potential in fairly electrovalent compounds[4] and effects of electronic relaxation on neighbour atoms[28] also contributing. Nevertheless, it is quite clear that $dI/dZ$ for different inner shells are shifted parallel along the vertical axis of Fig. 1 in agreement with the first-order hypothesis of one-shot ionization energies $I$ influenced by a HARTREE potential varying to almost the same extent for all the inner shells. Actually, $dI/dZ$ for $4d$ electrons is decreased by more than 70 percent in the lanthanides[26] compared with the neighbour elements, corresponding to the comparable average radii of $4d$ and $4f$ orbitals.

These results for inner shells clearly demonstrate the importance of interelectronic repulsion in attempting to discuss one-electron energies. Several paradoxes can be resolved considering the expression[29] for the energy including interelectronic repulsion in two shells $a^m b^n$

$$-mW_a - nW_b + \frac{m(m-1)}{2} J_{aa} + mn\, J_{ab} + \frac{n(n-1)}{2} J_{bb} \qquad (1)$$

which is readily generalized to three or more shells. $W_k$ is the ionization energy of the system containing only one electron (in the orbital $k$) besides the closed-shell core orbitals neglected in eq. (1). $J_{kq}$ is not exactly the $J$-integral between the squared wave-functions $k$ and $q$ but is slightly smaller. In the case of monatomic entities[3] the $J_{kq}$ of eq. (1) are the parameters $A_*(k,q)$. For two electrons in the same shell, $J_{kk}$ is approximately ten to fifteen times the spin-pairing energy parameter $D$. It is possible to consider $J_{kk}$ and $D$ as definite linear combinations of integrals of interelectronic repulsion to be evaluated for wave-function in a given approximation (*e.g.* that of HARTREE and FOCK) or to search the best representation of the experimental configuration baricenters in eq. (1) considered as a phenomenological baricenter polynomial[3].

Since the difference between the ionization energy and the electron affinity of the partly filled $3d$ or $4f$ shell (expressed by $J_{dd}$ or $J_{ff}$) easily can be above 10 eV, the situation[24] colloquially called "the third revolution in ligand field theory" can be related to eq. (1). Dr. JOHN AMMETER (ETH) was so kind as draw attention to the simple model system containing three electrons in two orbitals, of which the orbital having the largest ionization energy $W_a$ (after previous removal of two of the three electrons) represents the partly filled shell and is called $a$ in recognition of its anti-bonding character in "ligand field" theory, whereas the groundstate contains two of the three electrons in the orbital $b$. The four configuration baricenters of interest to us are:

$$\begin{aligned} E_0(b^2a^1) &= -2W_b - W_a + 2J_{ab} + J_{bb} \\ E_1(b^1a^2) &= -W_b - 2W_a + J_{aa} + 2J_{ab} \\ E_2(b^1a^1) &= -W_b - W_a + J_{ab} \\ E_3(b^2) &= -2W_b + J_{bb} \end{aligned} \qquad (2)$$

The electron transfer bands[30] having the wave-number $h\nu_{e.t.}$ and the photo-electron signals indicating $I(a)$ and $I(b)$ are the differences between the baricenters given in eq. (2):

$$\begin{aligned} h\nu_{e.t.} &= E_1 - E_0 = W_b - W_a + J_{aa} - J_{bb} \\ I(b) &= E_2 - E_0 = W_b - J_{ab} - J_{bb} \\ I(a) &= E_3 - E_0 = W_a - 2J_{ab} \end{aligned} \qquad (3)$$

A three-electron system of this kind known from atomic spectroscopy is the scandium atom[28] where the phenomenological parameters are $W_d = 24.75$ eV, $W_s = 21.60$ eV, $J_{dd} = 13.56$ eV, $J_{ds} = 8.38$ eV and $J_{ss} = 6.60$ eV corresponding to the three quantities of eq. (3) being 2.03, 6.62 and 7.98 eV when identifying $a$ with $3d$ and $b$ with $4s$. Said in other words, the groundstate $E_0$ of the neutral atom retains two $4s$ electrons as if the $3d$ orbitals were less stable, but the groundstate of $Sc^{+2}$ contains one $3d$ electron, and the energy level with one $4s$ electron outside the argon core has 3.15 eV higher energy.

The typical photo-electron results for volatile[22] and solid[27] compounds of the iron group are $I(a) = 12$ eV (the $d$-like orbitals) and $I(b) = 10$ eV (the loosest bound delocalized M.O.) whereas a typical[30] $h\nu_{e.t.}$ is 4 eV. Obviously, these three experimental values are insufficient to determine the five parameters of eq. (3) though they are compatible with $W_a = 24$ eV, $W_b = 21$ eV, $J_{aa} = 12$ eV, $J_{ab} = 6$ eV and $J_{bb} = 5$ eV. It is instructive to form the two linear combinations

$$\begin{aligned} I(a) - I(b) &= W_a - W_b - J_{ab} + J_{bb} \\ h\nu_{e.t.} + I(a) - I(b) &= J_{aa} - J_{ab} \end{aligned} \qquad (4)$$

showing that $J_{aa} \gg J_{ab} \sim J_{bb}$ produces $I(a) - I(b) \sim W_a - W_b$ and that as soon $(J_{aa} - J_{ab})$ is strongly positive, both $h\nu_{e.t.}$ and $I(a) - I(b)$ can be positive, in contrast to naive feelings.

If more than three electrons are considered in a system having the lowest configuration $a^m b^n$, eq. (3) is replaced by

$$\begin{aligned} h\nu_{e.t.} &= W_b - W_a + mJ_{aa} + (n-m-1)J_{ab} - (n-1)J_{bb} \\ I(b) &= W_b - mJ_{ab} - (n-1)J_{bb} \\ I(a) &= W_a - (m-1)J_{aa} - nJ_{ab} \end{aligned} \quad (5)$$

If $m$ increases, and $n$ is kept constant, $W$ arrives at unexpected large values out of all proportion with the observed $I$. Suppose the three $J$ parameters $J_{aa} = 12$, $J_{ab} = 6$ and $J_{bb} = 5$ eV remain constant, the measured $I(a) = 12$ and $I(b) = 10$ eV correspond to $W_a = 24 + (m-1)\,12$ and $W_b = 21 + (m-1)\,6$ eV somewhat in analogy to the apparent large contribution[31] of differential changes of the RACAH parameter $A$ to $\triangle$. It is interesting to note that the last line of eq. (4) remains valid in the more general eq. (5).

Though the higher $I$ of partly filled shells now is qualitatively understood, a major problem is the determination of L.C.A.O. eigen-vectors[24]. A consistent strategy is to apply the variation principle to eq. (1) including the interelectronic repulsion. We write our two orbitals to be used in the three-electron system

$$\begin{aligned} \psi_a &= (\cos\varphi)\,\psi_d - (\sin\varphi)\,\psi_x \\ \psi_b &= (\sin\varphi)\,\psi_d + (\cos\varphi)\,\psi_x \end{aligned} \quad (6)$$

with a parameter $\varphi$ in spite of this method apparently neglecting overlap integrals[4] between the central atom $d$ and ligand $x$ orbitals. A rather *ad hoc* apology for this convenient simplification is that the two orbitals may have been orthogonalized in an earlier step. In a system containing one $d$-like electron, the energy (including covalent bonding) may have been minimized at $\varphi = 20°$ giving the coefficients $\sin\varphi = 0.34$ and $\cos\varphi = 0.94$. In such a case, the stabilization of the bonding electron is $\mathrm{tg}\,\varphi = 0.364$ times the non-diagonal element of the effective one-electron operator. In the configuration $b^2$, the coefficients to the parameters of interelectronic repulsion are

$$(\sin^4\varphi)\,J_{dd} + (2\sin^2\varphi\cos^2\varphi)\,J_{dx} + (\cos^4\varphi)\,J_{xx} \quad (7)$$

with the numerical values 0.01, 0,20 and 0.79, respectively. If $J_{dx} \sim J_{xx}$ it is clear that eq. (7) only changes the optimal value of $\varphi$ to an insignificant extent. The situation is rather different for the configuration $b^2a^1$

$$[\sin^2\varphi(1+\cos^2\varphi)]\,J_{dd} + [2 - 2\sin^2\varphi\cos^2\varphi]\,J_{dx} + [\cos^2\varphi(1+\sin^2\varphi)]\,J_{xx} \quad (8)$$

where the three coefficients are 0.220, 1.794 and 0.986, respectively. Since the coefficient to $J_{dd}$ is only 0.130 for $\varphi = 15°$ but 0.325 for $\varphi = 25°$ and (exactly) 0.4375 for $\varphi = 30°$, the minimum energy for $b^2a^1$ is obtained for a lower degree of covalency in eq. (6) than if no a electrons are present. Actually the differential change of eq. (8) with $\varphi$ may very well over-compensate the one-electron effects of covalent bonding down to small values of $\varphi$.

It should be remembered that the configuration $b^2$ treated in eq. (7) is *not the lowest* of the two-electron system because $b^1a^1$ is more stable, and it is by no means obvious whether $\psi_a$ can be said in a consistent way to be the anti-bonding orbital. The situation is particularly alarming in the $4f$ group[24] where an upper limit (as derived from the nephelauxetic effect[3]) to the covalent bonding in the groundstate is $\varphi = 10°$, and $\varphi$ is probably below 5° in erbium (III) and ytterbium (III) compounds. Nevertheless, the ionized systems studied by photo-electron spectrometry have $I(4f)$ and $I$ of the ligands (say $2p$ of oxide or fluoride) almost degenerate, and hence $\varphi$ close to 45° is expected. Technically, this rearrangement of the coefficients to the eigen-vectors eq. (6) is a deviation from the behaviour[28] described by KOOPMANS. The photo-electron signals correspond to the eigen-states of the ionized system with adapted electronic density, as first explained by MANNE. Recently, this phenomenon has been verified for the many states of $4f^{q-1}$ formed by ionization of metallic lanthanides[32].

Since around 1958[2,31] it has been recognized that interelectronic repulsion is of major importance for energy levels described by "ligand field" theory. However, the emphasis was concentrated on parameters such as $D$ (approximately $7B$ for $d$ groups) explaining the promotion of electrons to anti-bonding sub-shells in many high-spin complexes. More recently, the $A_*$ or $J$ parameters (an order of magnitude larger than $D$) have attracted attention, the $4f$ and $3d$ groups having spectacular differences between $I$ and the electron affinity. This situation is also important for the relative stability of oxidation states.[3,33] However, a much more profound effect is the symphonical coupling of orbital energies *via* the two-electron operator necessitating at least a partial approach to HARTREE-FOCK calculations for the entire chromophore.

We now demonstrate that the later members of each $d$ group have anomalous low $I$ values of the partly filled shell, whereas the $4f$ group behaves in a more predictable way. Actually, the $I'(4f)$ values corrected for the huge spin-pairing energy can be extrapolated in a linear way from about 15 eV for lutetium (III)[24] back to some 8.5 eV for cerium (III) corresponding[34] to the parameter $(E - A) = 0.5$ eV. Since $D = 0.8$ eV, $I'(4f)$ is almost identical for Gd (III) and Lu (III), and marginally larger for $TbO_2$ than for $HfO_2$ corresponding to the chemical fact

[28] C.K. JØRGENSEN, *Adv. Quantum Chem. 8* (1973).
[29] C.K. JØRGENSEN, *Angew. Chem. 85* (1973) 1 [Intern. Ed. *12* (1973) 12].
[30] C.K. JØRGENSEN, *Progr. Inorg. Chem. 12* (1970) 101.
[31] C.K. JØRGENSEN, *Acta Chem. Scand. 12* (1958) 903.
[32] P.A. COX, Y. BAER and C.K. JØRGENSEN, *Chem. Physic. Letters 22* (1973) 433.
[33] C.K. JØRGENSEN, *Chimia 23* (1969) 292.
[34] C.K. JØRGENSEN, *Chem. Physic. Letters 2* (1968) 549.

that Yb(II) is easier to oxidize than Eu(II). In particular, the increase of $I'(4f)$ from $4f^{13}$ Yb(III) to $4f^{14}$ Lu(III) is 1.1 eV, much smaller than the increase 8 eV between the closed-shell systems Lu(III) and Hf(IV).

The situation is entirely different in the $d$ groups. As mentioned above, the jump of $I'(3d)$ is from 11 eV for Cu(II) to 16 eV for Zn(II) and $I'(4d)$ from 11 eV for Ag(I) to 17 eV for Cd(II). This sudden increase is far larger than the influence of the oxidation state; Co(II) and Co(III) have comparable $I'(3d)$, and $I'(4d)$ is marginally smaller for Rh(III) than for Pd(II). It is obvious that no description with a constant $(E - A)$ close to 1 eV as known from the standard oxidation potentials of the hexaqua ions[34] is compatible with the variation of $I'(3d)$ from 10 eV for $3d^6$ Co(III) to 26 eV for $3d^{10}$ Ga(III) though the variation is quite smooth from $3d^1$ to $3d^6$. A representative value for $3d^1$ is the gaseous titanium(III) hexafluoroacetylacetonate[22] with $I'(3d) = 7.94$ eV, and several solid $3d^3$ Cr(III) compounds are known to have $I'(3d)$ around 8 eV. This discrepancy becomes grotesque for higher oxidation states. Though $I'(4d)$ has not been measured for any Ru(VII) compound, it cannot be much higher than 9 eV in view of the chemical ionization energy[3,33] 5.5 eV derived from the standard oxidation potential of $RuO_4^-$ in aqueous solution, whereas it is 61 eV for $4d^{10}$ per-iodates[27]. Hence, keeping the oxidation state M(VII) constant, the average increase for each additional $4d$ electron is almost 6 eV. On the other hand, the typical variation of electron transfer spectra[30] in similar $d$-group complexes (of course excluding $d^{10}$) is 0.7 eV for each additional $d$ electron accompanied by $Z$ increasing one unit. This variation is related to the first line of eq. (5) and is not a simple function of the ionization energies.

The old-fashioned chemist smiles and says that it is obvious that the $d^{10}$ systems are essentially different from the partly filled $d$ shells. The photo-electron results for gallium(III) certainly do not encourage a simple "ligand field" description of $d^{10}$ as the standard of comparison. Though compounds of $3d^7$ nickel(III) and $3d^8$ copper(III) are known, and their photo-electron spectra are going to be discussed by STEGGERDA and us,[35] the easiest late M(III) to study is cobalt(III). Here, $I'(3d)$ is about 10 eV in salts of $Co(NH_3)_6^{+3}$ and lower, perhaps down to 8 eV, in sulphur-containing complexes.[27] The "vertical" ionization energy[19] of the lone-pair of gaseous ammonia 10.85 eV may be increased one or two eV by the coordination, so the inversion with higher $I$ of the partly filled shell does not seem to occur here. There is no doubt that the two-electron operator pulls in direction of less covalent bonding and less delocalization of the partly filled shell as discussed after eq. (8) and seen from the moderate nephelauxetic ratio 0.56 for $Co(NH_3)_6^{+3}$. This ratio[3] is approximately $(\cos^4\varphi)$ times the ratio between $J_{dd}$ in the modified central field (corresponding to the prevailing fractional charge) and $J_{dd}$ in gaseous $Co^{+3}$. Actually, the nephelauxetic ratio only approaches 0.25 in rare cases of $d^6$ chromophores such as $Rh(III)S_6$ and $Ir(III)Se_6$. Nevertheless, it is quite characteristic that in the approximation[3,36] of the fractional charge $z_{root}$ assigning equal parts (square-roots) of the nephelauxetic ratio to the expanded radial function (adapting to the modified central field) and to the delocalization, cobalt(III) complexes have $z_{root}$ below $+1$ (as a rare confirmation of the electroneutrality principle) to be compared with Cr(III) scattered between 2.5 and 0.6 or $MnF_6^{-2}$ having $z_{root} = 1.5$. We are forced by the photo-electron results to abandon the general idea from the M.O. treatment of molecules containing identical atoms (or at least atoms of comparable electronegativity) that the covalent bonding systematically increases $I$ of bonding M.O. The problem with fairly electrovalent molecules and polyatomic ions, and in particular $d$ and $f$ group complexes, is that the diagonal elements of one-electron energy change more under the influence of the varying fractional atomic charges than the effects of covalent bonding expressed by the non-diagonal elements. Since the total energy is minimized in the groundstate of the system, it is quite conceivable that it is an advantage to have lower $I$ of the $d$-like orbitals (concomitant with the lower fractional charge of the central atom) disregarding the apparent contradiction that the covalent bonding decreases $I$. Actually, the optical electronegativities derived from electron transfer spectra[30] show an unexpected irregularity of being 2.4 or 2.5 for high-spin Fe(III) to be compared with 2.35 for Co(III), quite in contrast to 2.1 for low-spin Ru(III) and 2.3 for Rh(III). It is possible that the former exception is a reminescence of the unusually low $I(3d)$ for Co(III) at least 1 eV lower than for Fe(III). The well-known propensity of strong bonding with ligands having lower electronegativity is indicated by the standard oxidation potential being $+0.1$ V for $Co(NH_3)_6^{+2}$ but $+1.8$ V for $Co(H_2O)_6^{+2}$. The corresponding chemical ionization energies 4.6 and 6.3 eV refer to adiabatic reactions, and it is known from crystallographic studies that the cobalt-nitrogen distances shorten to an exceptional extent by the oxidation. For comparison, the chemical ionization energy of $Fe(CN)_6^{-4}$ is 4.9 eV, not so much below $I'(3d)$ between 6 and 7 eV measured for various ferrocyanides.[27,37]

Another aspect of the crossing of $d$-shell and ligand $I$ values before zinc(II) is the contention of WILLIAMS[38] that copper(II) complexes are intrinsically highly covalent because of the high electron affinity of the last hole in the $3d$ shell. This opinion did not seem compatible with M.O. descriptions before it was now realized that the $I(3d)$ may jump rather dramatically from Cu(II) to Zn(II). However, another component of this situation is the specific (quadratic or square-pyramidal) stereochemistry of the highly stabilized copper(II) compounds.[12] When Cu(II) is closer to regular octahedral coordination the stabilization is much less pronounced.[13] Today, it does not seem too probable that covalent

bonding involving the $d$ shell is important in zinc(II). The resolution of the photo-electron spectra of solids is not good enough to indicate a separation of the five $3d$ orbitals, and it is not known whether the sign of the sub-shell energy differences is inverted. ELAND[39] has confirmed that the $I$ of the ligand orbitals are some 5 eV lower than of the $5d$ shell of several gaseous $HgX_2$. The chemical properties of Zn(II) are different from Mg(II) having a similar ionic radius, and it is tempting to ascribe covalent bonding to the empty $4s$ and perhaps the empty $4p$ orbitals. This problem becomes aggravated in silver (I) where $I(4d)$ and $I$ of the ligands almost coincide. By itself, this coincidence is expected to destabilize the compound in analogy to the repulsion between closed-shell cores. It has been suggested[4] that silver(I) complexes of ligands being "soft" according to PEARSON are stabilized by continuum effects like certain $d$ group complexes of phosphines and $PF_3$ which have no particularly evident reason to exist. A fundamental difficulty for the L.C.A.O. model is that it does not take weak deformations of the constituent atomic orbitals into account. However, Cu(I), Ag(I), Au(I) and Hg(II) may be specifically stabilized by the low-lying empty $s$ orbital. Thus, the differences in the logarithms of the formation constants of the linear complexes with two different pairs of ligands are 1.87 times larger[40] for gold(I) than for silver(I). This regularity is compatible with a strong mixing between the empty $s$ and the occupied, rotationally symmetric $d$ orbital in the linear chromophore XMX. The high excitation energy of this $5d$ orbital constituting the lone-pair perpendicular on the plane of $PtCl_4^{-2}$ is, most probably, also due to mixing with the $6s$ orbital.[4]

The arguments for "ligand field" stabilization in the hydration energy of $3d$ group ions[11,12] have an unexpected corollary in the mercury(II) and silver(I) aqua ions being unusually stable.[41] However, if the heats of hydration of the gaseous ions are divided by the square of the ionic charge, Al(III), Zn(II) and Ga(III) are situated between 43000 and 44000 $cm^{-1}$, slightly above the characteristic value for the $3d$ group[33] whereas Sc(III) has the value 37000 $cm^{-1}$ and both calcium(II) and yttrium(III) 33700 $cm^{-1}$ (these values are taken from Table 24 in ref. 2 revised to $H_h = 36$). It is very difficult to ascertain whether four of the ten $3d$ electrons of octahedral gallium(III) complexes are antibonding to any significant extent[10]. The change of hydration energy between $Sc^{+3}$ and $Ga^{+3}$ amounts to 8 eV, and it is very difficult to detect specific effects of 0.5 eV however much such a difference of free energy is of great interest for exchange of water with other ligands, representing a factor $10^8$ in the complex formation constants. A ninth of the hydration energy of $Co^{+3}$ is 42800 $cm^{-1}$ only slightly higher than 41100 $cm^{-1}$ for $Fe^{+3}$ and lower than $Ga^{+3}$. This agreement with "ligand field" arguments[12,13] coexists with the profound difference that $I'(3d)$ for Fe(III) and Co(III) are close to 10 eV like all the other compounds containing partly filled $d$ shells whereas four gallium(III) compounds[27] show the unexpected high value 26 eV. This contrast cannot be used as an argument for $d^2sp^3$ hybridization involving $3d$ orbitals[2,42] because the five $d$-like orbitals are non-bonding and anti-bonding in Fe(III), Co(III) and even Cu(II) and essentially non-bonding in Ga(III). The situation is rather different in thallium(III) alkyl complexes such as $Tl(CH_3)_2^+$ isosteric and isoelectronic with $Hg(CH_3)_2$, $Hg(NH_3)_2^{+2}$ and $Au(NH_3)_2^+$ where four $5d$ orbitals are non-bonding and one bonding by admixture with $6s$.

Other instances where it is possible to compare low-spin $d^6$ and $d^{10}$ systems in the same oxidation state are $PtCl_6^{-2}$ and $PbCl_6^{-2}$ or the recently prepared[43] gold(V) $AuF_6^-$ and $BiF_6^-$ where the crystallographic properties are similar with exception of the much smaller ionic radii of $d^6$. It is obvious that nickel(IV) and germanium(IV) are highly different both with respect to chemistry and photo-electron spectra, though both the chromophores[8] Ni(IV)$F_6$ and[35] Ni(IV)$S_6$ are known. In the latter case, the electron transfer bands have wave-numbers comparable to the "ligand field" transitions to the upper sub-shell, like in most quadratic gold(III) complexes. This coincidence indicates that the concentration of $d$-like character[42] is beginning to shift from the upper sub-shell to its bonding counter-part. Such a situation does not normally occur in cobalt(III), not even in chromophores[3] such as Co(III)$S_6$ and Co(III)$As_6$. On the other hand, the $3d$-like orbitals are distinctly below the ligand orbitals (though they have $I$ comparable with oxygen $2s$ and lower $I$ than fluorine $2s$) in gallium(III), whatever that means to the chemist. It might be argued, as for the extent of covalent bonding in lanthanides, that the ionized situation of a given central atom should be related to the oxidation state one unit higher. In this case, it is $I(3d)$ of zinc(II) being larger than $I$ of the loosest bound ligand orbitals which can be compared with the chemistry of the trivalent $3d$ elements. Contrary to partly filled $d$ shells, $3d^{10}$ has $I$ strongly dependent on the oxidation state (like[26] closed-shell $4f^{14}$) and $I' = 8.9$ eV for CuCN and $I = 8.93$ and 9.55 eV, respectively, for gaseous[44] $Ni(CO)_4$ and[45] $Ni(PF_3)_4$. The lower sub-shell has $I = 9.76$ and

[35] J.J. STEGGERDA, J. WILLEMSE, C.K. JØRGENSEN and H. BERTHOU, under preparation.
[36] C.K. JØRGENSEN, *Helv. Chim. Acta, Fasc. extraord. Alfred Werner 1967*, 131.
[37] J. FENGER, C.K. JØRGENSEN and H. BERTHOU, under preparation.
[38] R.J.P. WILLIAMS, *Disc. Faraday Soc. 26* (1958) 123.
[39] J.H.D. ELAND, *Int. J. Mass Spectr. & Ion Physics 4* (1970) 37.
[40] C.K. JØRGENSEN and J. POURADIER, *J. Chim. Physique 67* (1970) 124.
[41] E. SCROCCO and O. SALVETTI, *Ricerca Scientifica 24* (1954) 1258 and 1478.
[42] C.K. JØRGENSEN, *Chimia 25* (1971) 109.
[43] K. LEARY and N. BARTLETT, *Chem. Comm.* (London) *1972*, 903.
[44] D.R. LLOYD and E.W. SCHLAG, *Inorg. Chem. 8* (1969) 2544.
[45] J.C. GREEN, D.I. KING and J.H.D. ELAND, *Chem. Comm.* (London) *1970*, 1121.

10.58 eV in these two molecules. Said in other words, some $d^{10}$ systems are more transition-group-like than others.

*Note added in press.* The first case of higher $I$ for $d$-like electrons reported[46] seems to be $Mn(CO)_5X$ for X = Cl, Br and I. A recent case[47] of gaseous $ZnX_2$ show $I(3d)$ = 19.02, 18.69 and 18.39 eV, respectively. These values perceptibly higher than for solids[27] suggest larger relaxation effects in condensed matter.[28] M.O. calculations[48] on quadratic $CuCl_4^{-2}$ show the twelve Cl-3$p$-like orbitals with $I$ between 1.5 and 5.3 eV, the half-filled Cu 3$d$ at 12.5 eV and the four other 3$d$ orbitals between 12.2 and 13.7 eV whereas gaseous $FeF_3$ considered[49] as an equilateral triangle is calculated to have nine F 2$p$ type orbitals with $I$ between 16.6 and 18.3 eV and, somewhat extremely, the five half-filled orbitals between 26.6 and 27.7 eV. The next $I$ = 40.9 eV represents F 2$s$. These results look more ionic than the photo-electron spectra of solid iron(III) compounds.

*Acknowledgements*

I would like to thank my colleagues at Anorganisch-Chemisches Laboratorium, ETH Zürich for many discussions about this problem, and Dr. BERTHOU for careful measurements on the Varian IEE-15 photo-electron spectrometer provided by the Swiss National Science Foundation (grant 2323-70).

[46] S. EVANS, J.C. GREEN, M.H.L. GREEN, A.F. ORCHARD and D.W. TURNER, *Disc. Faraday Soc. 47* (1969) 112.
[47] B.G. COCKSEY, J.H.D. ELAND and C.J. DANBY, *Trans. Faraday Soc. II* (1973) 1558.
[48] J. DEMUYNCK, A. VEILLARD and U. WAHLGREN, *J. Amer. Chem. Soc. 95* (1973) 5563.
[49] R.W. HAND, W.J. HUNT and H.F. SCHAEFER, *J. Amer. Chem. Soc. 95* (1973) 4517.