The Distinction Between Anti-bases (Electron-pair Acceptors) and Oxidizing Species (Electron Acceptors) *

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Dedicated to Professor Bernard Susz on occasion of his 70th birthday (5.10.74)

Summary

Electron pairs, as first discussed by Kossel and Lewis, are not as easy to identify with coordinative links in bridged halides and complexes with high coordination number. The fractional atomic charges evaluated for approximate wave-functions do not help much in this respect, whereas the classificatory aspects of oxidation states derived from spectroscopic properties and stereochemistry may be significant. The coordination number of uranium (IV) is discussed.

In the time interval between the hydrogen atom model of Niels Bohr sixty years ago and actual quantum mechanics now fifty years old, two ideas were emitted almost simultaneously which influenced all chemists profoundly. Kossel[1] pointed out most of the stable oxidation states of elements outside the transition groups are isoelectronic with noble gases, such as N(−III), O(−II), F(−I), Na(I), Mg(II), Al(III), Si(IV), P(V), S(VI) and Cl(VII) isoelectronic with neon. At the end of each transition group, similar series occur, such as Fe(−II), Co(−I), Ni(0), Cu(I), Zn(II)... now known up to Br(VII) or Yb(II), Lu(III), Hf(IV), Ta(V), W(VI), Re(VII) and Os(VIII) not corresponding to noble gases. In a few instances, even two additional *s*-electrons produce chemically stable series such as Tl(I), Pb(II) and Bi(III). Many crystals containing members of these isoelectronic series with charges from −1 to +3 seem pretty electrovalent, but it cannot be argued that all compounds of this class are ionic. Thus the oxo and fluoro complexes of the high oxidation states look rather covalent, and the negative and zero oxidation numbers of the transition groups are only known with specific ligands such as CO and PF_3. Lewis[2] suggested that all the valence lines connecting two atoms in chemical formulae correspond to electron pairs responsible for the covalent bonding. By the same token as deviations from the coordination number $N = 4$ in carbon compounds are satisfactorily explained by double and triple bonds, it is necessary to introduce one (CH_3^-, NH_3), two (NH_2^-, H_2O) or three (OH^-, HF) lone-pairs to keep the number of adjacent electron-pairs invariantly 4. This classification works admirably for carbon, nitrogen and oxygen compounds but many difficulties occur for N above 4, and extreme cases[3] are oxides, nitrides and carbides cristallizing in NaCl type with six equivalent neighbour atoms and the colourless (or at most, amber-yellow) fluorite-type Be_2C where carbon has $N = 8$.

* Received March 6, 1974.

Subsequently, two parallel theories for *acidities* were developed. Brønsted considered the transfer of a proton as the fundamental reaction,[4] and the solvents capable of shielding acid-base reactions are those where a characteristic acid is constituted by the adduct of one proton with a neutral solvent molecule. Whereas the detailed neighbourhood of H_3O^+ in aqueous solution (as contrasted to crystalline perchlorates and *p*-toluenesulphonates of this cation) is rather uncertain[5] and that such species only subsist for a very short time, a good case of a proton adduct is NH_4^+ in liquid ammonia. Lewis wanted a much more general treatment of acids and suggested that the essential property is their capability of accepting electron pairs donated by bases. Seen from a historical point of view, it was clear that *anhydro-acids* show acidic properties and can neutralize indiscutable bases. Thus, CO_2, SO_2 and OsO_4 can add OH^- increasing N in species such as $HOCO_2^-$, $HOSO_2^-$ and $OsO_4(OH)_2^{-2}$ which may further deprotonate, *e.g.* to CO_3^{-2}. In the symmetric description suggested by Arrhenius of H^+ and OH^- as the characteristic ions in water, NH_3 was also a problem and was later called an anhydro-base. It is clear that a sufficient condition for possibly being an acid according to Lewis but not according to Brønsted is to contain no mobile protons, such as the anhydro-acids, whereas any Lewis base is potentially a Brønsted base being able to add a proton. The common class of bases is the reason why Jannik Bjerrum[6] proposed to call the Lewis acids *anti-bases* being able to neutralize, to react with bases. One may discuss a few marginal cases. Thus, the proton affinity of CO in the gaseous state is not much higher than of krypton or xenon atoms and comparable to diatomic HCl and HI, but it may also be argued that (with exception of H_3BCO) the CO ligands in complexes are Lewis acids rather than bases, accepting *d*-electron density from the central atom. Already Brønsted pointed out that the two related reactions

$$\begin{aligned} 2\,H^+ + 2\,e^- &= H_2 \\ H^+ + H^- &= H_2 \end{aligned} \qquad (1)$$

are the inevitable link between acid-base and redox reactions, inspiring the subversive question whether the electron is a kind of base. Thus, when aqueous acid is neutralized with metallic magnesium, one may argue that crystals containing Mg^{+2} and conduction electrons are a base because of the latter constituent.

The chemists would like to distinguish clearly[7] between electron donors (reducing species) and electron-pair donors (Lewis bases). At one hand, it is perfectly clear that F^- and NH_3 rather belong to the latter category, but present quantum chemistry makes the distinction less clear-cut in many cases. Since Werner introduced the concept *coordination*, it is true that books[8,9] classify complexes according to ligands (such as NH_3, F^-, $P(C_6H_5)_3$ and I^-) which can be recovered, and only very rare examples (O_2, O_2^-, O_2^{-2}; NO^+, NO, NO^-; certain sulphur-containing ligands[10]) do not suggest a well-defined charge of the ligand recovered. However, one should not be trapped by the automatic classification by conditional reflexes, and the reason why ammonia complexes of cobalt(III), rhodium(III) and iridium(III) are thus classified is not the easy recovery of NH_3 but absorption spectra and other low-spin d^6 characteristics. An extreme case of impossible recovery is the discovery by Delépine that iridium compounds deprotonate NH_4^+ in boiling sulphuric acid to dark green $NIr_3(SO_4)_6(H_2O)_3^{-4}$ containing[11,12] one Ir(III) and two Ir(IV) bound to the central nitride known as unidentate ligand in $NOsO_3^-$.

Seen from the point of view of the organic chemist the question how to apply coordination concepts is whether it is a better approximation to leave the Lewis electron pair to the more electronegative partner by heterolytic bond-breaking (H_3CCF_3 to CH_3^+ and CF_3^-) rather than divide the electron pair homolytically (to CH_3 and CF_3 in the example). It would not be practical to consider loosely bound complexes of ammonia and chloride as derivatives of NH_3^+ and Cl, nor bridging chloride as Cl^+. In cases of comparable electronegativity, the two opposite directions of heterolysis (CH_4 to CH_3^+ and H^- or to CH_3^- and H^+; CH_3I to CH_3^+ and I^- or CH_3^- and I^+) can both be defended, producing the ackward question[13] whether pyramidal $Te(CH_3)_3^+$ contains tellurium(IV) like $TeCl_3^+$ (isoelectronic with $SbCl_3$ and $SnCl_3^-$) or tellurium (−II). It is necessary to make a distinction between physical metallicity (being a question of the electric resistivity being roughly independent of the absolute temperature T, or, as in typical metals, proportional to T, but not strongly decreasing like in semi-conductors) occurring not only in most elements and in alloys, but also in stoichiometric compounds[10] such as LaS, ThS, $CuRh_2S_4$ and LaI_2, and the chemical properties characterizing metallic elements. It is well-known that chemical metallicity is a pronounced function of the oxidation state. Thus, Cr(VI) and Mn(VII) are closely similar to S(VI) and Cl(VII) whereas the behaviour of Cr(III) and Mn(II) is analogous to Al(III) and Mg(II) with exception of the absorption spectra and magnetic properties. A typical non-metallic (let us here use the old word metalloïd) characteristic is the chasing away of protons from aqua ligands forming hydroxo and oxo ligands. It is possible[9] to introduce the oxidation state divided with the ionic radius as a parameter to describe, together with pH, the occurrence of these three ligands. The consecutive pK values of protons bound to the same atom differ strongly, such as 17 units between H_3O^+ and H_2O as Brønsted acids in water. The protonated and deprotonated forms of phosphoric acid $P(OH)_4^+$, $OP(OH)_3$, $O_2P(OH)_2^-$ and O_3POH^{-2} have an equidistant series of pK values −3, 2, 7 and 12 showing the influence of adjacent hydroxo ligands. The parameter (z/r) is so high for Cl(VII) and Os(VIII) that only oxo ligands occur in aqueous solution. This description must accept a few exceptions, such as the co-existence of aqua and oxo ligands in $VO(H_2O)_4^{+2}$ and UO_2^{+2}. Quite generally, the central atoms soft in the sense of Pearson[14] such as Cl(I), Br(I), Pd(II), I(I) and Hg(II) have aqua ions more acidic than one would expect from their values of (z/r).

It is well known that water or ammonia coordinated to gold(III) and platinum(IV) have low to moderate pK values readily forming complexes of OH^- and NH_2^-. By the same token, protonated methanol $CH_3OH_2^+$ has an acidity comparable with hydrated protons, and methylammonium $CH_3NH_3^+$ is a marginally weaker Brønsted acid than NH_4^+. The organic chemist would not normally think about these two species as an aqua and ammonia complex of carbon(IV) but there is the important content in this description that other carbonium ions such as $C(C_6H_5)_3^+$ are anhydrous and anhydro-acids by forming the carbinol $(C_6H_5)_3COH$ which would be called a leuko-base in dyestuff chemistry[15]. The molecule $(C_6H_5)_3CCl$ dissolves in organic solvents[7] and reacts with $SbCl_5$ loosing Cl^- to form $SbCl_6^-$. This brings us to an important point of certain molecules functioning as Lewis bases to a point being stretched too much and forming related anti-bases by loosing a halide anion. Thus, acetyl fluoride CH_3COF might react with BF_3 like a multitude of other oxygen-containing molecules such as ketones and ethers, but it actually rearranges to the BF_4^- salt of CH_3CO^+. The analogous formyl cation HCO^+ is not known, as discussed in the beginning.

It is not always easy to make a clear distinction between asymmetric halide bridges and salt formation. In condensed matter (solutions, vitreous and crystalline solids) there is always some other atoms in a given direction, and considerable interest is attached to the rare cases of interatomic distances in the interval between normal chemical bonds and the much longer distances determined by Van der Waals interactions. Such intermediate distances sometimes correspond to strong hydrogen bonds[16] and in other cases to physical metallicity[17]. In analogy to adducts between a Brønsted acid and its corresponding base (such as FHF^-) anti-bases frequently react with fractional amounts of base. Molten aluminium chloride contains $Cl_2AlCl_2AlCl_2$ (this molecule consists of two joined tetrahedra like B_2H_6 but in contrast to rectangular I_2Cl_6 and Au_2Cl_6) and reacts with excess Cl^- to form tetrahedral $AlCl_4^-$ like

the quadratic ICl_4^- and $AuCl_4^-$. However, with a smaller amount of Cl^-, the $Al_2Cl_7^-$ formed probably has one chloride bridge isosteric with $S_2O_7^{-2}$. In aqueous solution, it is obvious that the number of ligands either increases or stays constant as a function of increasing concentration of the free ligand. This statement is less clear-cut in molten salts. Thus, the absorption spectrum of UCl_4 in aluminium chloride gives the impression of the chromophore $U(IV)Cl_8$ compatible with bridged species such as $U(Cl_2AlCl_2)_4$ or $U(ClAlCl_3)_8$. This bridging may be compared with the pink modification of $U(H_3BH)_4$ syncrystallized in hafnium(IV) borohydride[18] whereas green undiluted $U(BH_4)_4$ has $N = 14$. Other examples of high coordination number of uranium(IV) is $N = 16$ in the cyclopentadienide $U(C_5H_5)_3Cl$ and the cyclo-octatetraenide $U(C_8H_8)_2$. When CsCl is added to the solution in Al_2Cl_6 having $N = 8$, *N decreases* to six in octahedral UCl_6^{-2}.

Other instances of a partly neutralized anti-base are $FXeFXeF^+$ (a symmetric, bent adduct[19] of XeF^+ and XeF_2) and recently[20] detected $FKrFKrF^+$. When preparing salts such as $XeF^+SbF_6^-$ or $XeF^+TaF_6^-$ it is never certain before the crystal structure is known whether halide-bridging such as XeFTa occurs. Actually, dinuclear anions such as $F_5SbFSbF_5^-$ and the corresponding platinum(V) fluoro complex are also cases of partly neutralized anti-bases, and the reaction between gaseous PtF_6 and Xe reported by Bartlett in 1962 is now known to produce a mixture of $XeF^+PtF_6^-$, $XeF^+Pt_2F_{11}^-$ and $Xe_2F_3^+PtF_6^-$.

Like high external pressure, the choice of non-aqueous solvents can be seen from the electron transfer spectra[21] to decrease the MX distance[22] in octahedral MX_6^{+z-6}. Whereas the mixed chloro-bromo complexes $UCl_{6-x}Br_x^{-2}$ can be studied in nitromethane[23] it was previously thought that UF_6^{-2} could not exist. Crystalline double fluorides[24] with the stoichiometry A_2UF_6 are fluoride-bridged with $N = 8$ or 9. However, tetra(alkyl)ammonium fluoride in propylene carbonate[25] dissolves UF_4 as UF_6^{-2}. The success of this solvent is partly connected with decreased U—F distances and partly by the absence of hydrogen bonding between the solvent and the rear side of the fluoro ligands. A comparable situation is known with lanthanide MCl_6^{-3} which were previously known in solution mixtures of acetonitrile and succinonitrile[26] and in highly hygroscopic salts of large organic cations, but which have now turned up to exist[27,28] in the cubic crystal Cs_2NaMCl_6.

Though more or less approximate quantum-mechanical calculations are not in particularly good shape for polyatomic molecules and ions, at least it has been made clear that the distinction between coordinative (dative) and conventional covalent bonds does not depend on an objective property of the individual wave-function. The question is not here the mode of formation (say BF_3 reacting with F^- or NH_3) or way of dissociation of a complex, but the static properties of the groundstate. In the same way as the *preponderant electron configuration*[10] serves to define the (spectroscopic or conditional) oxidation state, one may look for higher-type properties in the sense of Bertrand Russell. It cannot be argued that a complex such as H_3BNH_3 in an absolute sense contains B^- and N^+ though the molecule is the final result of a perturbation of moving one proton from one carbon nucleus to the other in ethane. This can, at most, counteract the usual tendencies toward distribution of fractional atomic charges in the same way as CO tends toward C^- and O^+ in order to retain the triple bond known from the isoelectronic nitrogen molecule, or cristalline GaAs a tendency toward Ga^- and As^+ in order to remain analogous to Ge. In both cases, the atoms in the actual groundstate are roughly neutral, whereas the isoelectronic BF molecule and solid CuBr have the charge separations expected from relative electronegativity[29]. Daudel[30] also agrees that the classification of H_3BNH_3 as a coordination complex is a higher-type property based on the optimized probability for the presence of two electrons in spatial regions called "loges". This recognition of moderate fractional atomic charges (even after inclusion of the Madelung potential[10,29]) makes the distinction between electron-pair donors and reducing electron donors difficult. The other way round, it is clear to the chemists that certain anti-bases are not oxidizing electron acceptors to any significant extent, *e.g.* boron(III) and aluminium(III) compounds. This argument should not be swept under the rug in the general acceptation of most central atoms having accessible empty orbitals producing affinity for ligands and oxidizing character.

Recently, Jannik Bjerrum[31] suggested to compare anti-bases with their adducts with an electron pair, somewhat in analogy to corresponding Brønsted acids acids and bases differing by a proton. Some such pairs are fairly straightforward, such as I^+ and I^- or the simplest conceivable, H^+ and H^-. Many oligo-atomic systems change stereochemistry to a large extent, such as planar SO_3 and pyramidal SO_3^{-2}; B_2H_6 with two hydride bridges* compared with $B_2H_6^{-2}$ isosteric with ethane; tetragonal-pyramidal $Mn(CO)_5^+$ considered part of octahedral $Mn(CO)_5X$ compared with trigonal-bipyramidal $Mn(CO)_5^-$. It is typical[10] for sulphur, chlorine and all the post-transition group elements that the oxidation number has the same parity as the atomic number, or said in other words, the corresponding gaseous ion contains an even number of electrons. The same is true for some of the last transition group elements, such as palladium and gold. These changes two electrons at a time are frequently accompanied[13] by characteristic changes in N and symmetry.

Several attempts[31,32] have been made to correlate formation constants of complexes in aqueous solution

* This is less unexpected than the perovskite $BaLiH_3$ containing each hydride bound octahedrally to two lithium (I) and four barium (II).

with the hard and soft character of the anti-bases and bases according to Pearson[14]. Among the bases, OH^- does not possess a well-defined position like hard F^- or soft I^-, RS^- and R_3P. As far as goes H^+_{aq} as anti-base, it is rather on the soft side, having high affinity to CN^- and even more so to CH_3^- and H^- (the latter anion is an interesting case of a soft ligand without possibilities for back-bonding to discrete, empty orbitals. Like phosphines and PF_3, it may be a case[33] of continuum effects, which also show up as decreased ionization energies measured in photo-electron spectra[34]). This interpretation needs the lower pK of HCl than HF and of H_2Te and H_2S than of H_2O to be explained by specific solvation effects on the deprotonated anions.

Many authors speak about electrons as if they have a specific attraction making them occurring in pairs. There is the truth in this statement that the high values of S for a large number q of electrons [the possible total spin quantum number being $S = 0, 1, 2, 3 \ldots (q/2)$ for even q and $S = {}^1/_2, {}^3/_2, {}^5/_2, \ldots (q/2)$ for odd q] are not known in practice. Already in the gaseous lithium atom, the lowest level with $S = {}^3/_2$ (belonging to the configuration $1s2s2p$) though metastable is high up in the continuum above the groundstate of Li^+. However, in systems containing two or more orbitals with identically or approximately the same energy (as is true for C_2^+, O_2 and most transition-group compounds) containing 2, 3, ... electrons, but two less than the maximum, the spin-pairing energy originating in interelectronic repulsion[29,33] produces the *lowest* energy for the highest S compatible with the occupation of the degenerate orbitals. Organic molecules (with exception of $C(C_6H_5)_3$ and $[(CH_3)_3C]_2NO$ and related species) contain an even number of electrons and show $S = 0$ either because they have low symmetry without degenerate frontier orbitals or because there is a large gap between the highest filled and the lowest empty orbitals, as is the case for methane. This fact cannot be translated to a tendency of chemical bonds each corresponding to a definite pair of electrons, and it is much more important that the standard form of recoverable ligands normally has $S = 0$ than that it contains definite lone-pairs able to coordinate, though it is true that photo-electron and electron transfer spectra[21] frequently show ionization or excitation energies of orbitals essentially being lone-pairs. Recently, ten different dilemmas and paradoxes in quantum chemistry[35] were discussed with particular emphasis on possible restrictions on the validity of the Copenhagen interpretation. Though the most appropriate object for quantum mechanics has remained the structure of line spectra of monatomic entities, there is no doubt that the understanding of chemical bonding hesitantly starts at a primitive but promising level.

Acknowledgements. The present paper is the last by the writer before his translocation to Département de chimie minérale et analytique. The writer would like to express his gratitude for having been selected as a successor to Professor Susz and also for the most pleasant five years in the Département de chimie physique, where all the five sub-departments are so different and do so much to promote the development of the individual scientist.

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