Coordination Chemistry Reviews, 26 (1978) 33—45

NEW COORDINATION CHEMISTRY OF SATURATED LIGANDS

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Received 20 June 1977

The foundations of coordination chemistry were laid on studies mainly of complexes of saturated ligands. The same subject matter served for developing and testing principles governing the dynamics of reactions in solution, and, as comprising the main descriptive content of qualitative analysis, it contributed to the training of several generations of chemists in the practical application of equilibrium principles. In the new wave of interest in coordination chemistry which began in about 1950, the chemistry of the complexes of saturated ligands was again prominently featured. Early in this phase, the systematic studies of a number of fundamental aspects of coordination chemistry began, and initially at least these dealt almost exclusively with complexes of saturated ligands. Among such studies were those devoted to hydration of cations and so-called electron transfer reactions, to substitution reactions, including isomerizations, and as an important new field, those requiring rapid reaction techniques. Finally, it should be noted that the ideas of electronic structure, expressed in crystal and ligand field theory, were fashioned to account for the electronic spectra, magnetic properties and structures, again of complexes mainly of saturated ligands.

The early development of the chemistry of the complexes of water and ammonia is of course a consequence of their being accessible by reactions in the convenient and abundant solvent water, without resort to highly specialized techniques. The early history of the subject of aquo and ammine complexes saw a great elaboration of the preparative aspect, while in the later phase, synthesis was secondary to attempting to systematize and understand the chemistry. In the interim since 1950, the field of organometallic chemistry, in which unsaturated ligands play a central role, has grown enormously, and just as in the early stages of the development of the chemistry of so-called classical complexes [1], an interest in new syntheses has predominated. Although this growth, in terms of new significant compounds being prepared, has overshadowed that registered for classical complexes, it has enhanced rather than diminished the significance of saturated ligand chemistry. Concern with the qualities of ligands, how their properties are modified by coordination, and how a particular ligand affects other components of a complex, has come very much to the fore. Saturated and unsaturated ligands affect properties in different ways and it is necessary to understand ligand effects over the whole range of ligand characteristics if the full potential of coordination chemistry for controlling reactivity is to be realized. In fact, a major part of the article will be devoted to describing the interplay between saturated and unsaturated ligands in an area of chemistry which makes a systematic investigation of it feasible. But a rather general title was chosen for this article because the field of coordination chemistry can only benefit if the dichotomy which now exists — some studying only organometallic compounds and others only classical complexes — disappears. Because saturated ligands are so commonplace, they tend to be overlooked by practitioners of organometallic chemistry, and at the present time their chemistry, rather than that of unsaturated ligands, seems to stand in need of advocates. In line with responding to this need and of justifying the general title, the major theme will be prefaced by an outline of some areas in the field of saturated ligand chemistry which seem to have potential for further development.

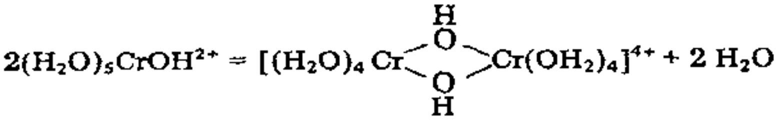
Before proceeding with this, something needs to be said about the system of ligand classification being used. The qualities of the ligands which need to be considered are their capacities to form σ bonds by donation, π bonds by donation, and π bonds by accepting electron density from the metal atoms or ions. Interactions between these three effects are also undoubtedly important. With six parameters to consider, and with ligands possessing these qualities to differing degrees, ligand classification is a complex subject, and of necessity, in what follows, gross simplifications will be adopted. Ammonia and water, and closely related molecules will be used as exemplary of saturated ligands. For ammonia, it seems likely that the important bonding effects arise from σ donation to the metal regarded as a Lewis acid. For water, however, there is a pair of electrons which can act by π donation to the metal, and the tendency for such donation is expected to increase on deprotonation. Our interest will be limited to middle-period transition metals in the 3+ and 2+ oxidation states, and thus oxide ion is not an important ligand for present purposes. The effect of π donation from the ligand is overlooked in the common classification of ligands as a saturated vs. unsaturated. It is undoubtedly important in understanding ligands as common and useful as OH^- and Cl^- and it deserves systematic treatment and investigation in its own right, but it will be largely ignored in what follows. Carbon monoxide will often be used as exemplary of unsaturated or π acid ligands. Classifying it as unsaturated or as a π acid focusses attention on its capacity to accept π electron density, though it is tacitly recognized that σ and π donating effects are present as well. The capacity of CO for σ donation is usually much less than that of NH_3, but in the face of the strong interaction between CO and BH_3, it would be imprudent to make a sweeping statement covering the comparison.

We turn now to a catalogue of areas in saturated ligand chemistry which, either because they represent obvious gaps in knowledge or because they have been opened up by recent discoveries, come to notice as having a potential for development. No claim to completeness is made. As already mentioned, only species in oxidation state 3+ and 2+, where H_2O can be expected to be a ligand at moderate acidity, will be considered, and even within this limited scope, significant issues will undoubtedly have been overlooked.

For the first row transition metal ions, the aquo complexes are by now rather well characterized, in the sense that formulas are known, structures usually are known, and substitution labilities have been determined. There remains the necessary but virtually endless task of determining the involvement of the solvent in complexes in solution. Among the second row transition elements, mono-nuclear aquo or ammine ions are less abundant. Substitution—inert species are particularly interesting and much remains to be done on the reactions and properties of species such as $Ru(H_2O)_6^{2+}$ [2], $Ru(H_2O)_6^{3+}$ [3], $Rh(H_2O)_6^{3+}$ [4], $Ir(H_2O)_6^{3+}$ [5] and $Pd(H_2O)_4^{2+}$ [6]. Several aquo ions of this general category remain to be prepared. Among them are those derived from Os(III), Pt(II) and Au(III), but it is doubtful that the last two would resist condensation long enough to survive ordinary preparative methods. While many of the properties of the species can be predicted, their chemistry, once it is investigated, is sure to provide some surprises, and it is impossible to foresee, based on what we now know, just what new chemistry the aquo species might lead to. An important additional incentive for continuing the investigations acknowledges the importance of the aquo solvent system, and therefore of the complexes that are intrinsic to it. It is doubtful if mono-nuclear complexes in either the 2+ or 3+ state will be accessible in the aquo or ammono system for Tc [7], Re or W. Species containing Nb [8] in the oxidation state 3+ have been described for aqueous solutions containing only SO_4^{2-} as an extraneous stabilizing ligand. These species merit study, and the prime issue is to learn whether any among them is mono-nuclear [9]. A search needs also to be made for conditions under which Zr(III), known to exist in solid halides [10,11], might persist in water and related solvents, and it is not at all clear that the possibility that lower oxidation states of Ta and Hf can also persist, has been excluded by previous research.

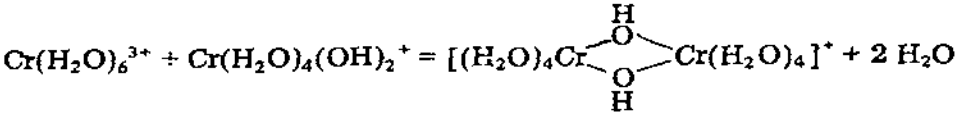
The roster of aquo bi-metal complexes was considerably expanded by the characterization of $Rh_2^{4+}aq$ [12] and $Mo_2^{4+}aq$ [13]. At issue in their preparation was less the question of whether they might exist than whether they would persist long enough to be preparable by orthodox methods. The species $Rh_2^{4+}aq$ is likely to be unstable in the equilibrium sense with respect to the metal and $Rh(H_2O)_6^{3+}$ — a disproportionation reaction of some kind is in fact induced by NH_3 [14] — and $Mo_2^{4+}aq$ in acid is likely to be unstable with respect to H_2 and molybdenum in a higher oxidation state. The facile preparation of $Mo_2^{4+}aq$ is unfortunately no guarantee that the analogous tungsten complex will prove tractable [15]; the latter is expected to be more reactive than the former toward oxidation, both in the kinetic and thermodynamic sense. It does seem likely however that Ir_2^{4+} aq is accessible, though it will probably be more strongly reducing than is $Rh_2^{4+}aq$. The only remaining homonuclear bi-metal species for which there seems to be any likelihood that an extensive aquo chemistry can be developed is Re_2^{6+} [16], but there may be some opportunities among bi-metal heteronuclear combinations. Though no aquo ions of this type have been prepared, the existence of tetracarboxylate of the Mo(II)—W(II) combination [17] suggests that it is reasonable to search for analogous aquo ions. Of special interest for the heteronuclear species is the equilibrium stability with respect to disproportionation to the homonuclear combinations, and of concern, the kinetic stability. If the species can be prepared, the question of equilibrium stability can readily be answered at least approximately by thermochemical measurements. No opportunities have come to light for aquo or ammine polynuclear species, homo- or hetero- without intervention of ligands bridging the metal—metal bonds.

In the foregoing, only species were considered in which bridging groups are not involved in the metal—metal interactions. When even simple bridging groups such as OH^-, O^{2-}, and halide ions are considered, an extremely large field is opened for the binuclear combinations alone. These have already been extensively, though by no means exhaustively, investigated, and of course polynuclear combinations in great abundance have also already been dealt with. A recurrent issue in such cases is just what the stability of union owes to the bridging group. In fact, even for the most common case, that involving OH^- as bridging group, it is not easy to understand why a species such as the so-called "chromic dimer" is as stable as it is. The equilibrium constant for the reaction



$$2(H_2O)_5CrOH^{2+} = [(H_2O)_4\,Cr\begin{matrix}\overset{H}{O}\\ \underset{H}{O}\end{matrix}Cr(OH_2)_4]^{4+} + 2\ H_2O$$

is 4.6×10^2 at 37.5° [18] and this seems remarkably high considering that ions of the same charge are being brought together. (Expressed in the "chelating" form



$$Cr(H_2O)_6{}^{3+} + Cr(H_2O)_4(OH)_2{}^{+} = [(H_2O)_4Cr\begin{matrix}\overset{H}{O}\\ \underset{H}{O}\end{matrix}Cr(H_2O)_4]^{+} + 2\ H_2O$$

the equilibrium quotient would be a factor of approximately 10^2 greater.)

The important studies by Bradley [19] and coworkers showed that substituting OH^- as a ligand by OR^- leads to striking changes in stability and in chemistry. Contributing to the differences is the greater resistance of OR^- to heterolysis, and the opportunities provided for introducing steric effects by the proper choice of R. The lessons to be learned from these discoveries seem not to have been applied systematically in solution chemistry. To cite a possible application: it seems very likely that in methanol as solvent, the life time of Mn^{3+} can be greatly prolonged. In an application of this kind, methanol has two advantages over water: lower temperatures are accessible in it, and oxide ion, which in stabilizing Mn(IV) provides a driving force for the disproportionation of Mn^{3+} in water, can be extracted from methanol only with great difficulty. In other applications, such as in searching for lower oxidation states, the greater resistance of methanol to reduction can be exploited. Methanol has the serious limitation that it is less resistant than water to oxidizing agents, but despite this it seems likely that there is an extensive chemistry to be explored in alcohols as solvent media. There may also be opportunities in solvents such as phosphate esters, which do not readily yield anionic coordinating ligands, and will therefore modify the chemistry still further.

The importance of polydentate ligands has been widely appreciated since the pioneering researches of Bjerrum [20] and Schwarzenbach [21], but their potential for producing novel changes in properties is far from exhausted. Particularly inviting are the opportunities they offer for imposing an unusual coordination environment on a metal ion. The high affinity of several polar groups acting in cooperation can be exploited by forcing on the metal ion interactions which could not be realized in the monodentate mode. This interaction can take the form of an unusual arrangement of the polar groups themselves, or of bringing a weakly nucleophilic (saturated hydrocarbon) segment next to the metal ion. The full potential of the especially interesting class, the macrocyclic ligands, is not realized when the rings are fully saturated, but even the fully saturated ones modify both rate and equilibrium reactivity in quite surprising ways. Illustrating the former is the stability of the Co(III)—alkylide bond [22] and the remarkable inertia of some carbonato complexes to decomposition by acid [23] when Co(III) is complexed by a saturated macrocyclic. As to the latter, there are a number of oxidation states, ordinarily very strongly oxidizing, which become stable in a macrocyclic environment [24]. In this connection, the observations reported by Margerum and coworkers [25] which show that Cu(III) is easily formed when it is coordinated to tetraglycine, are instructive. It may well be that the stabilization of higher oxidation states by macrocyclic ligands owes less to the ring structure than it does simply to providing a source of saturated nitrogen bearing a negative charge, while avoiding the complications that accompany the metal ion chemistry of simple amides or imides. Cryptands are a special class within an already special class. The remarkable properties reported for the Co(II)—Co(III) couple as the sepulchrate [26] suggest a wealth of additional possibilities for stabilizing unusual oxidation states and for modifying properties.

The isoelectronic series of saturated ligands: F^-, H_2O, NH_3, extrapolates to CH_3^- as the next member. Though methylide and other alkylide ions are saturated ligands, they have no share in the "classical" era of the coordination chemistry of the middle-period transition elements, this chemistry being much too recent. The species now known embrace "super" methylated or anionic species [27] permethylated [28] and peralkylated neutral molecules [29], and species which contain, in addition to an alkylide ion, ordinary saturated ligands such as water or ammonia. Remarkable among these is the series with alkylide coordinated to the pentaaquochromium(III) series, the first of which was prepared by Anet and LeBlanc [30], and which continue to be the subject of intensive investigation. Those based on cobaltammines have already been mentioned. Closely related is $Rh(NH_3)_5C_2H_5^{3+}$, a species which is very stable in water [31]. The series will undoubtedly be extended, and if the requirement that the species be preparable by orthodox methods is removed, a large number of different metal ion—alkylide complexes will be available for study (vide infra).

In the preceding, preparability by orthodox procedures has been emphasized, though an interest in the properties of the substances, including reactivity, has been implicit in the discussion. It needs to be emphasized that the influence of metal ions on reactivity, even for the class of saturated ligands is a major field in its own right. The classic studies by Buckingham, Sargeson and coworkers on metal-assisted nucleophilic substitution [32], show that even without resorting to exotic compositions, striking chemistry is encountered. Though much of modern homogeneous catalysis now concerns itself with organometallic combinations, it must be borne in mind that many important biological processes involve hydrolyses and condensations in the presence of water on metal ions as commonplace as Mg^{2+} or Zn^{2+}, and are extensions of aquo ion chemistry.

When a substance can be prepared by orthodox methods, this at once implies that it persists for a period long compared to that required for separation, in at least one of the phases. It is of course convenient and for many purposes essential that a species meet this kind of criterion. But many reaction intermediates, important though they are, by their very nature cannot do so. The importance of intermediates having metal—hydrogen bonds in aqueous solution chemistry was convincingly demonstrated by Halpern's studies [33], and species formed by the interaction of carbon radicals with transition metals by, among others, Kochi and coworkers [34]. Unusual oxidation states are encountered in abundance in the study of oxidation—reduction reactions. These intermediates become reactants in their own right when pulse methods are used for generating them. Pulse radiolysis is a particularly powerful method of generating unstable species. The chemistry accompanying radiolysis of water can be adapted to provide solvated electrons (which react with transition metal ions in the 2+ state to produce the unstable 1+ species [35]), hydroxyl radicals (which produce higher oxidation states), atomic hydrogen or carbon radicals. In a recent study [36] which illustrates the power of the method both CrH^{2+} (formed by the reaction of Cr^{2+}aq with atomic hydrogen) and Cr^{+} (formed by the reaction of Cr^{2+}aq with e^{-}aq) are described. A large number of important species, including the class of hydrolytic intermediates, probably fall within the scope of ordinary rapid mixing techniques [37]. A successful application of this experimental approach has been made by Schwarzenbach and coworkers to the characterization of $Cr(OH)_3$ as a mononuclear species [38].

We turn now to the issues which arise in the study of complexes containing both saturated and unsaturated ligands. To simplify matters, we will be concerned mainly with extreme compositions, on the one hand those species in which unsaturated ligands preponderate, and on the other, those with the inverse composition ratio. The issues to be considered are of the same kind in both composition extremes, and they will be illustrated with respect to a specific example.

In a molecule such as $Mo(CO)_5ROH$, the quality of the $Mo(CO)_5$ unit acting as a Lewis acid is of importance. Though Mo is in a formal oxidation state (0), because the CO groups are presumed to be electron withdrawing, $Mo(CO)_5$ may be quite a strong Lewis acid. What then is the acidity of water attached to Mo(0) (methanol may be needed as a substitute for H_2O)? Is it possibly as great as that of water in $Mo(H_2O)_6^{3+}$? The particular question raised bears on the relative affinities of H_2O and HO^- for $Mo(CO)_5$ but it is of interest to explore the relative affinities of other saturated ligands for the Lewis acid, and of course to include unsaturated ones in the comparison. The effect of the saturated ligand on the complementary ones is also at issue. How is the lability of the Mo—CO bond altered when CO in $Mo(CO)_6$ is replaced by a saturated ligand? Are the effects different in *cis* and *trans* positions? Similar questions will be raised in the discussion, to be undertaken presently, of systems in the other extreme in composition.

What work has been done with carbonyl-rich mixed ligand complexes has until recently been sporadic rather than systematic, but this situation seems now to be changing [39,40]. There are of course limitations on the investigations imposed by instability. Saturated ligands favor higher oxidation states (note that among middle-period transition elements there are no stable aquo or ammine complexes of oxidation state (1+)) and the mixed carbonyl—saturated ligand complexes are subject to disproportionation. In spite of this thermodynamic instability, a large field for investigation is open at least for the octahedral pentacarbonyl species where the disproportionation reactions are often quite slow. The species $Cr(CO)_5NH_3$ [41], $Mo(CO)_5NH_3$ and $W(CO)_5NH_3$ [42] have been prepared by reactions in aqueous solution and are remarkably resistant to attack by the solvent. Many similar combinations with other saturated ligands in place of NH_3 have been prepared by photochemical means, among them $Cr(CO)_5NEt_3$, $W(CO)_5NEt_3$ [43], and an analogous alcohol complex [44]. Species with higher ratios of saturated to unsaturated ligands are known — thus $W(CO)_4L_2$ has been reported [45] and $Cr(CO)_3(NH_3)_3$ as well as other similar compositions [46] for the Group VI series. The analogous tris-aquo complex does not appear to exist, and instead has been obtained only in the condensed form in the solid [47]. Whether the tendency to condense reflects partial metal—metal bond formation, or whether it reflects some special effect of the metal—tricarbonyl radical on the OH group, remains to be understood.

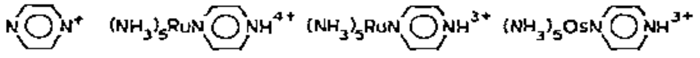
The ammine and aquo complexes of ruthenium(II) and osmium(II) readily lend themselves to a systematic investigation of the issues raised earlier, as these are manifested in the high saturated/unsaturated ligand composition ratio. The propensity which these complexes have for back-bonding interactions is dramatically illustrated by two kinds of observations. One concerns the stability of the complexes with di-nitrogen. The reactions

$$Ru(NH_3)_5OH_2^{2+} + N_2 = Ru(NH_3)_5N_2^{2+} + H_2O$$

$Ru(NH_3)_5OH_2^{2+} + Ru(NH_3)_5N_2^{2+} = [Ru(NH_3)_5]_2N_2^{4+} + H_2O$

are governed by equilibrium constants of 3.3×10^6 and 7.3×10^3 respectively (25°, standard state for solutes, molarity) [48]. Because of the instability of $Os(NH_3)_5OH_2^{2+}$ in water — E_f for the $Os(NH_3)_5OH_2^{3+,2+}$ couple is −0.97 v [49] — the equilibria with dinitrogen cannot be studied directly in this case. Nevertheless, it has been demonstrated that there is formation of $[Os(NH_3)_5]_2N_2^{4+}$ by continued electrolytic reduction of an aqueous solution of $Os(NH_3)_3Cl^{2+}$ in the presence of $Os(NH_3)_5N_2^{2+}$ [50]. In terms of current ideas of bonding, the replacement of the water dipole from the dipositive cation by the neutral molecule, N_2, is understood by invoking back donation. Of the reasonably stable aquo species, the only other candidate for direct reaction with N_2 appears to be Cu^+aq. The interaction of N_2 with Cu^+ can readily be studied by determining the increase in the concentration of Cu(I) in equilibrium with Cu(s) + Cu^{2+}aq when N_2 is added to the system. This increase with N_2 at 1 atm was observed [51] to be less than 5% (the experiments should however be repeated with N_2 under pressure), and the affinity of Cu^+aq for N_2 appears to be considerably less than that of $Ru(NH_3)_5H_2O^{2+}$.

That Ru(II) and Os(III) have a special interaction with π acid ligands is demonstrated also by the values of pK_a for the series



pK_a = 0.6 [52] −0.8 [53] 2.5 [53] 7.4 [50]

The response of pK_a to placing $Ru(NH_3)_5^{3+}$ on the pyrazinium ion reflects the inductive effect of the cation, which enhances the acidity. However, while $Ru(NH_3)_5^{2+}$ is also cationic, coordination by it to the pyrazinium ion decreases the acidity substantially — and for $Os(NH_3)_5^{2+}$ the analogous effect amounts to seven orders of magnitude. The increased basicity of the ligand on being coordinated to Ru(II) and Os(II) is attributed to back-bonding; the electron density transferred from metal to ligand by this mechanism is great enough to overcome the purely inductive effect of the charge.

Elsewhere, the case for concluding that back-bonding interactions are important for Ru(II) [54,55] and Os(II) [55] when a single saturated ligand has been replaced by an unsaturated one, has been developed. Since the reasons for the interactions being so prominent for just these ions have already been dealt with [55], they will be discussed here only briefly. An essential point is that Ru(II) and Os(II) have the low spin d^6 electronic configurations, and this is optimum for back-bonding in octahedral complexes. The fact that Ru(II) and Os(II) exist with only saturated ligands coordinated to them is also essential — to maximize the back-bonding interaction to a particular π acid ligand, the complementary ligands should not be unsaturated, because such ligands would compete for πd electron density. Finally, considering the πd^6 configuration as a function of oxidation state, we note that for the 3+ oxidation state, back-bonding is much diminished compared to the 2+, and though it would be greater for the 1+ state than for the 2+, very few complexes of the type $(NH_3)_5Mt(I)Ln$ [56] exist (one example is *trans*-$Tc(NH_3)_4(H_2O)NO^{2+}$ [7].

Though Cu(I) features strong back-bonding interactions, the complexes of Ru(II) and Os(II) are much more suitable for the purposes of a systematic investigation of the effects resulting from it. The latter, but not Cu(I), form substitution—inert combinations, especially with unsaturated ligands, and compositions and structures can be inferred with a great deal of confidence even for species in solution. It should also be noted that in contrast to the high carbonyl composition regime for mixed complexes, in the high saturated ligand regime, the introduction of the unsaturated heteroligand probably stabilizes the complex with respect to disproportionation. At any rate, as will appear, species of the type $(NH_3)_5Mt^{II}Ln$ can be generated in great abundance for Ru(II) and Os(II). In the case of ruthenium, most can be prepared even in aqueous solution where the unsaturated ligand competes with the nucleophilic solvent for a position in the coordination sphere. Owing to the instability of aquopentaammineosmium(II), less direct preparative methods are needed to generate the members of the Os(II) series.

Among the complexes of the class $(NH_3)_5Ru^{II}Ln$ which have been characterized, in addition to species already mentioned, are those with Ln = CO [57,58], N_2O [59], nitrile [60], pyridine and related ligands [53], pyrazine [53], methyl pyrazinium ion [61], $P(OR)_3$ [62], SO_2 [63], H_2S [64], $S(CH_3)_2$ [64], $Se(CH_3)_2$ [65], $Te(CH_3)_2$ [65], ethylene [66,67] and acetylene [66,67]. In every case mentioned except for N_2O, replacement of water in $Ru(NH_3)_5OH_2^{2+}$ takes place substantially completely with the ligand at ordinary, say 0.1 M, concentration. The summary of equilibrium data accumulated for a number of ligands, including also saturated ones, and including also the data for $Ru^{III}(NH_3)_5Ln$ as shown in Table 1 is instructive.

Several items in this tabulation are especially noteworthy. The unsaturated

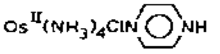
TABLE 1

Equilibrium constants for the replacement of water by various ligands (aqueous solution, 25°)

Ligand[a]	$Ru(NH_3)_5H_2O^{2+}$	$Ru(NH_3)_5H_2O^{3+}$	Ratio	Ref.
N_2	3.3×10^4	4.0×10^{-13}	8×10^{16}	48
Thiophene	~ 10	$\sim 2.5 \times 10^{-8}$	4×10^8	64
H_2S	1.5×10^3	2.4×10^{-4}	6×10^6	64
$(CH_3)_2S$	$\geqslant 10^5$	$\geqslant 1.6 \times 10^{-2}$	$\sim 6 \times 10^6$	64
Pyridine	2.4×10^7	6.0×10^3	4×10^3	68
Imidazole	2.8×10^6	1.9×10^6	1.5	69
NH_3	3.5×10^4	1.6×10^5	2×10^{-1}	68
Cl^-	0.4	1.1×10^2	4×10^{-1}	70, 71
HS^-	1.5×10^6	2.4×10^{13}	6×10^{-8}	64
HO^-	6.0×10^2	6.0×10^{11}	1×10^{-9}	64

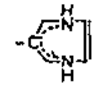
[a] Standard state, molarity.

ligands, and among these we count N_2, H_2S, $(CH_3)_2S$ and pyridine, have a high affinity for Ru(II), but of them, those with a very poor σ-donating capacity have an extremely low affinity for Ru(III). The low affinity in these cases is expected, if in fact, back-bonding is a minor interaction in the higher oxidation state. Among the sulfur donors, the relatively weak coordinating ability of thiophene toward Ru(II) comes to attention, as does the fact that the affinity to Ru(III), which more nearly measures the σ base strength of the ligand, is extremely low. Finally, the very low acidity of $Ru(NH_3)_5OH_2^{2+}$ ($pK_a \sim 13$) reflected in the association constant of Ru(II) for OH^- shows that Ru(II) does not have much capacity to exploit the polarizability of a ligand in coordinating to it. The contrast to Hg^{2+}, which has a very high affinity for both OH^- [72] and Cl^- [73] ($\log K = 11.3$ and 6.74 respectively) is very striking.

A property of the Ru(II)—Ln combination which is useful both in helping to understand the interactions, and in applications, is the absorption which they show attributable to a πd—π^* charge transfer transition [53]. The corresponding absorption bands usually have high extinction coefficients, of the order of 10^4 M^{-1} cm^{-1}. For the nitrogen heterocyclics, the absorption is in the convenient visible region of the spectrum. The analysis of the spectra [74] for a series of complexes $Ru^{II}(NH_3)_5Ln$ and *cis* and *trans* $Ru^{II}(NH_3)_4Ln_2$ with Ln common to series, has led to an estimate of the stabilization of the Ru^{II}—Lr bond by back-bonding. The value of 4.4 kcal thus obtained is in reasonable agreement with other estimates [74]. Application of the same methods to osmium complexes shows, as expected also on other grounds, that back-bonding is more important for Os(II) than for Ru(II); in fact, analyses of the observations for  leads to the conclusion that in the ground state, a πd electron pair is more than 50% delocalized onto the unsaturated ligand [75]. The enormous increase in the basicity of the coordinated pyrazine already referred to is in accord with this conclusion.

In the case of Ru(II) some systematic work has been done on the effect of a π acid ligand on other ligands in the same molecule. For a large number of such ligands including N donors and some sulfur donors, the effects seem to be rather easy to understand on the basis that unsaturated ligands drain electron density from the metal ion. When an ammonia in $(NH_3)_5Ru^{II}L$ is replaced by an unsaturated ligand, the lability of L is decreased if L is saturated, but increased when L is unsaturated [76]. For the unsaturated ligands in the cases so far studied, the weakening of the bond thus implied is in fact reflected in a decreased thermodynamic stability [64,76,77]. The kinetic effects referred to are much the same in *cis* and in *trans* positions [76].

Much more difficult to understand are ligands which labilize both saturated and unsaturated ligands *trans* to them. (In the case of SO_3^{2-} as the *trans* labilizing, it has been shown that it actually delabilizes in the *cis* position when the leaving group is H_2O [77].) This class includes, in addition to SO_3^{2-},

CN^- [78], $P(OR)_3$ [62] and  [76]. In the case of SO_3^{2-}, this labilizing effect has proven to be very useful in preparative work [76,77,79].

Much of the research referred to in the latter part of this article, apart from its usefulness in understanding back-bonding, and in the case of the last group of ligands, in exposing interactions which are not as yet clearly formulated, should be regarded as preparation for the study of the reactivity of the coordinated ligands. This very important aspect has not yet been attacked systematically, and is an inviting prospect for future work, particularly with complexes of osmium(II), where, owing to the large amount of charge transfer, dramatic effects can be expected.

Another worthy goal is to extend the range of species in which ligands ordinarily featured in organometallic chemistry are found to be compatible at least in the sense of kinetic stability, with saturated ligands within the same molecule. Particularly appealing, and still to be explored, are open face sandwhich combinations in which a radical such as cpMt is forced to adopt saturated ligands to complete the coordination about the metal. Access to this kind of chemistry for at least one combination, $C_6H_6Ru^{2+}aq$ [80], is provided by the compound [$\pi - C_6H_6RuCl_2$] [81]. Apart from the intrinsic interest in chemistry of this kind, there is the practical goal of realizing new catalytic processes, perhaps even polymerizations leading to C—C bond formation in the convenient and abundant solvent water.

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