Coordination abilities in aqueous 1:1 metal chelates of 1,3-dicarbonylic ligands: absolute hardness and absolute electronegativity

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For a series of monochelates of metal and oxo-metal ions such as Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, VO^{2+}, and UO_2^{2+} with structurally similar 1,3-dicarbonylic ligands it has been found that the logarithms of stability constants are essentially linear functions of the ligand pK. Correlation data show that for a given transition metal ion it is possible to estimate approximate stability constants of a wide range of 1,3-dicarbonylic monochelates and, therefore, predict overall equilibrium constants.

Results have provided information concerning absolute hardness and absolute electronegativity of the metal ion considered against the stability of 1:1 chelates in aqueous solution.

Introduction

Metal complexes in solution may be roughly classified on the basis of the speed with which equilibrium between metal ion and ligands is attained. Those which attain it rapidly are described as "labile", those which attain it slowly as "inert". Both aspects of the equilibrium, *speed of attainment* and *position*, are important for a proper understanding of the behavior of metal complexes in solution.

The reactivity of the metal ion toward a ligand in aqueous solution is closely bound up with the nature of the metal ion and ligand (solvation and ionisation degree, stereochemistry, *etc.*) and an understanding of it and of its relationship with other properties is fundamental to the interpretation of the stability of a metal complex.

During the last few years, complexation between metal or oxo-metal ions and 1,3-dicarbonylic ligands to form mono-chelated complexes has seen renewed interest from a kinetic[1] point of view (*speed of equilibrium attainment*). These ligands have become quite useful, not only as tools in chemistry; they are also of practical importance, both with regard to current health issues[2] (intermediates in the preparation of HIV inhibitors) and other more traditional aspects[3] (*e.g.*, control of soil-borne fungi, insecticides, fluorescence production, solvent extraction, *etc*). As part of the continuing interest in these complexation reactions, this work will study some important features in relation to equilibrium *position*. The idea of Hard and Soft Acids and Bases developed by Pearson, which has been used as a unifying principle in several texts,[4–6] might be expected to be able to predict equilibrium constants of metal complexes in aqueous solution. An achievable objective might be to develop quantitative scales of metal-hardness, or any other property or parameter, for predicting expected behavior of complexation reactions in a single important medium such as aqueous solution.

Results and discussion

Dissociation constants of the ligands, $K = [H^+][L^-]/[HL]$, where HL is the undissociated ligand and L^- is the enolate ion, were determined potentiometrically[8] by titrating solutions of the ligand having concentrations in the range 1.0×10^{-3}–1.0×10^{-2} mol dm^{-3} with standard sodium hydroxide solutions in a double-walled titration cell under an atmosphere of nitrogen

gas. Data treatment was carried out using the program SUPERQUAD.[9] With this program the dissociation constant of the ligand is determined by minimisation of an error-square sum based on measured electrode potentials. Since compounds of this class readily undergo cleavage in alkaline solution, for the less acidic ligands it was thought desirable to check these results by the Method of Parallel Straights[10] through spectrophotometric measurements. Standard buffer solutions were prepared in a pH range close to the pK of the ligand. The wavelengths were selected at regular intervals around the absorption maximum of the ligand (270 to 315 nm). The averaged pK values of the ligands at 25 °C are shown in Table 1.

The compositions of the complexes have been investigated spectrophotometrically using the method of continuous variations introduced by Job[11] and also by the method of Yoe and Jones.[12] Results obtained from the above methods are in good agreement with each other, and they indicate a 1:1 stoichiometry. Finally, a COMIC plot was used. COMIC is a computer program[13] which can calculate the equilibrium concentrations of each entity (both free and complexed species) in a multicomponent system of metal ions and ligands.

The stability constants of the monocomplexes, $\beta = [ML^{(n-1)+}]/[M^{n+}][L^-]$ were determined potentiometrically by titrating solutions of the 1:1 chelates with standard sodium hydroxide solutions. The SUPERQUAD[9] computer program was used for data treatment.

In other cases β was determined spectrophotometrically through a conditional constant β' and the Schwarzenbach coefficients.[14] β' was determined from absorption values at the stoichiometric point according to Job's method.

The overall equilibrium of complex formation, which may be expressed as eqn. (1), was obtained spectrophotometrically.

$$K_{ML} = \frac{[ML^{(n-1)+}][H^+]}{[M^{n+}][HL]} \qquad (1)$$
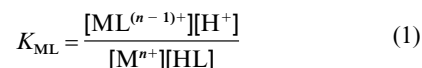
The range of hydrogen ion concentrations was high enough to prevent high degrees of hydrolysis/polymerisation in cases such as iron(III) and chromium(III). The solutions contained such an excess of metal ion that only the 1:1 complex was formed. The absorption change at a fixed wavelength, where the mono-chelated complex absorbs strongly, is a function of the equilibrium constant, and the metal, ligand and proton concentrations used [eqn. (2)].

Table 1 The ionization constants (pK) of a series of 1,3-dicarbonyl ligands and the stability constants for the corresponding monochelate compounds formed with Ni^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, VO^{2+}, and UO_2^{2+}

Chelating agent	pK	log β						
		Co^{2+}	Ni^{2+}	Cu^{2+}	Cr^{3+}	Fe^{3+}	VO^{2+}	UO_2^{2+}
Pentane-2,4-dione	9.01	5.13[a]	5.92[b]	8.26[c]	10.1	10.5	8.74[d]	7.74[e]
Hexane-2,4-dione	9.39				11.0	10.9		
Heptane-3,5-dione	10.0			8.52	11.9	11.8	9.39	7.70
2,6-Dimethylheptane-3,5-dione	11.0	6.39	7.20			12.7		
6-Methylheptane-2,4-dione	9.21				10.9	11.1		
2,2,6,6-Tetramethylheptane-3,5-dione	12.0				14.2	14.1		
Octane-2,4-dione	9.94					11.3		
Nonane-2,4-dione	10.0					11.5		
1-(2-Thienyl)butane-1,3-dione	8.40					10.0		
1,1,1-Trifluoropentane-2,4-dione	6.11	3.50[f]	4.10[f]	5.72[f]	6.70	6.60		
4,4,4-Trifluoro-1(2-thienyl)butane-1,3-dione	6.39	3.55[g]	4.30[g]	5.52[g]	9.20	7.02	5.90[d]	5.54[h]
2-Acetylcyclopentanone	8.10				9.20			
2-Acetylcyclohexanone	10.3				12.1	11.9		

[a] Ref. 28. [b] Ref. 29. [c] Ref. 30. [d] Ref. 31. [e] Ref. 32. [f] Ref. 33. [g] Ref. 34. [h] Ref. 35.
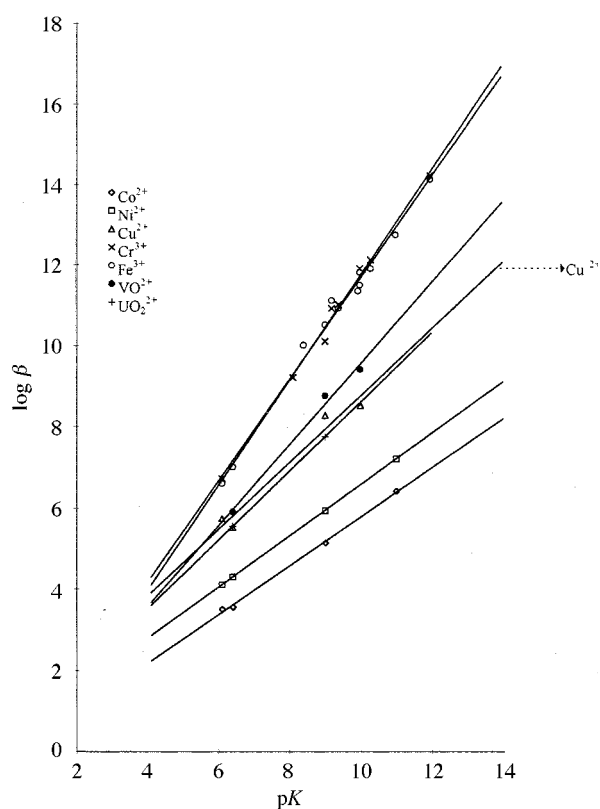

Fig. 1 The stability constants of complexes of several metal ions with structurally similar 1,3-dicarbonylic ligands as a function of the corresponding ligand ionization constants (pK).

$$[HL]/A = [H^+]/([Fe^{3+}]\varepsilon K_{ML}) + 1/\varepsilon \qquad (2)$$

From an appropriate analysis of the data, using a correlation of the ratio [HL]/A vs. the ratio [H$^+$]/[M^{n+}], K_{ML} may be readily determined.[15]

The stability constants of the monocomplexes, β, can also be calculated indirectly from the relationship $\beta = K_{ML}/K$, and their values agree quite well with those obtained experimentally.

Fig. 1 presents a plot of the log β values for a series of monochelate complexes against the negative logarithm of the ligand ionisation constants.

When considering reactions between a particular metal ion and ligands of general structure R^{1}COCH$_2$COR^2, results show that stability constants of metal chelates are dependent upon the properties of the substituents, R^1 and R^2. If we analyse the substituent effect of alkyl groups on the stability constants of alkyl, alkyl substituted β-diketonates, it can be seen that the equilibrium constant decreases as the inductive effects of the alkyl groups increase. In the case of trifluoro derivatives, 1,1,1-trifluoropentane-2,4-dione and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione, in which the CF$_3$ group is electron-withdrawing through an inductive effect, it is likely that the σ and π systems are strongly perturbed and the reduced electron density causes a smaller chelating effect than in metal chelates which contain alkyl groups (i.e. pentane-2,4-dione, heptane-3,5-dione).

The factors which control the ring strain of 2-acetylcycloalkanones would influence the relative stabilities of their respective complexes. From these results it can be argued that the reduced ring strain in 2-acetylcyclohexanone may increase the stability of the condensed double hexacycle chelate, compared to five- to six-membered chelate rings in 2-acetylcyclopentanone (i.e. chromium derivatives). Furthermore, the relative stabilities of two enol forms (endo- and exo-cyclic) are strongly influenced by the ring size and it is usually accepted that the exo-enol is more stable than the endo-enol for five-membered ring systems and vice versa for the six-membered ring systems.[16]

An analysis of what we have called equilibrium position could also be useful. In fact, Fig. 1 shows a relation between the acidity of a particular 1,3-dicarbonylic ligand and the stability of its monochelates. As a general rule, it could be expected that a strongly acid diketone gives an anion which is a poor donor and transfers little charge to the metal atom; conversely a diketone with a high pK transfers considerable charge, with the result that the metal chelate is more stable.

An overall examination of the results in Fig. 1 shows that complexation reactions seem influenced, at first, by the hard or soft acid character of the metal species involved. There are a variety of kinds of experimental data for classifying metal ions and oxo-metal ions as being hard acids, soft acids or borderline.[17–20] Hard acids are usually of high positive charge and small size, and do not have easily excited outer electrons. Soft acids have acceptor atoms of low positive charge, large size and several easily excited outer electrons and hence are very polarisable. Those ions considered borderline have an intermediate behavior.

In a complexation reaction, polarisability means deformation of an electron cloud in the presence of other atoms or groups to which bonding is occurring. The criterion used is that hard acids form more stable complexes with the donor atoms of various bases in the general order of decreasing electronegativity: F > O > N > Cl > Br > C > . . . Looking at this list of donor atoms, it is obvious also that polarisability increases

Table 2 Experimental parameters for monoatomic cations arranged in order of increasing I, A and χ. Oxo-cations such as VO^{2+} and UO_2^{2+} are considered Hard (H) on the basis of the HSAB classification of the Lewis acid from Pearson[17] (B = Borderline)

Metal	I/eV[a]	A/eV[b]	χ/eV	η/eV	d^n	$E°$/V	r^+/Å[c]	HSAB
Co^{2+}	33.50	17.06	25.28	8.22	d^7	−0.28	0.72	B
Ni^{2+}	35.32	18.17	26.75	8.58	d^8	−0.25	0.69	B
Cu^{2+}	36.84	20.29	28.57	8.28	d^9	0.35	0.57	B
Cr^{3+}	49.10	30.96	40.0	9.10	d^3	−0.71	0.53	H
Fe^{3+}	54.80	30.65	42.73	12.08	d^5	−0.04	0.55	H

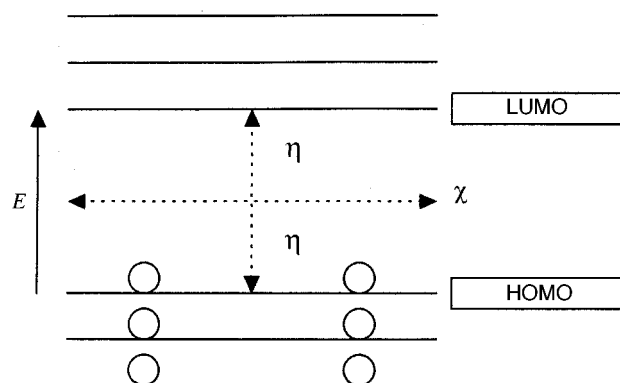[a] Ref. 36. [b] Ref. 37. [c] Ref. 24.

Fig. 2 Orbital energy diagram showing χ and η for a filled shell molecule.

as one goes to the right. Thus, the donor atom in β-diketones as hard base presents an electron cloud that is difficult to deform chemically. The general statement: "hard acids prefer to coordinate to hard bases, and soft acids prefer to coordinate to soft bases" (the HSAB Principle) may be used to rationalise the results in Fig. 1. The interpretation lines in Fig. 1 are a reasonable physical model of how HSAB behaviour can arise. It can be seen that, in general, the slopes of the lines (log β *vs.* p*K*) increase when metal-ion hardness increases.

In fact, over the years a variety of scales of hardness have been proposed. Recent works based on the Density Functional Theory[21] have developed the concepts of absolute electronegativity and absolute hardness from the definition of electron chemical potential [eqn. (3)], where E is the electronic energy of

$$\mu = (\delta E/\delta N)_v \simeq (I + A)/2 = -\chi \qquad (3)$$

a molecule, atom, or ion, N is the number of electrons, v is a fixed set of nuclear charges, I is the ionisation potential, and A is the electron affinity.

It was accordingly suggested that χ be called Mullikan's electronegativity, which is also equal to the electronic chemical potential, μ, with a change in sign. The quantity $(\delta\mu/\delta N)_v$ might be related to the idea of hardness, η [eqn. (4)].

$$\eta = 1/2(\delta\mu/\delta N)_v = 1/2(\delta^2 E/\delta N^2) \simeq (I - A)/2 \qquad (4)$$

The properties I and A also have a special significance when using an orbital description of a chemical species. According to Koopmans' theorem,[18] the frontier orbital energies are given by: $-E_{HOMO} = I$ and $-E_{LUMO} = A$.

Fig. 2 shows the usual orbital energy diagram for a filled shell molecule. χ is shown as a broken horizontal line on the diagram. It is just the average of the HOMO–LUMO energies, with a change in sign. The hardness, η, is shown as a broken vertical line. The HOMO–LUMO gap is equal to twice the value of η. This gives a new insight into the meaning of hardness. A hard molecule is characterised by a large HOMO–LUMO gap. A soft molecule has a small gap.[22]

Table 2 shows χ and η for bare cations, but of course we must deal with metal ions surrounded by various solvent molecules. There is an important effect of solvation to consider. The I and A values, which are used to calculate χ and η, are gas phase values, however in solution we should use the corresponding values, I' and A' [eqns. (5) and (6)].

$$M(aq) \rightleftharpoons M^+(aq) + e^-(g) \quad I' \qquad (5)$$

$$M(aq) + e^-(g) \rightleftharpoons M^-(aq) \quad A' \qquad (6)$$
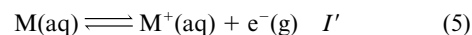
One use for solution-phase values of I' and A' is to calculate absolute electronegativities, χ', and hardness parameters, η', in solution. If we know I and A in the gas phase for the species M, we can calculate I' and A' from the free energies of hydration,[23] but no data were available for the species under study.

Although the discussion based on our results in aqueous solution has some limiting factors, such as the low number of data points, these results are in quite good agreement with the gas phase data in Table 2, and perhaps could make some contribution to a better understanding of the effect of the metal and the ligand on the stability of chelate compounds. However, some adjustments in correlative studies may be needed when considering cations with too different hard/soft properties.

Considering the results for dipositive metal ions, traditionally considered borderline in the hard–soft classification, copper(II) complexes are a case where the hardness effect appears to be particularly high (Fig. 1). Even its stability constants are of the same order of magnitude as those assigned to oxo-metal ions considered hard (*e.g.* UO_2^{2+} and VO^{2+}). This large hardness effect is not reproduced in the reactions of any other dipositive metal ion.

One of the reasons may be that the ability to accept transferred charge, and hence to stabilise the metal ion, should be related to the standard electrode potential of the metal in aqueous solution. The reduction potential of Cu^{2+} (+0.35) is considerably greater than the reduction potential of any other 3-d transition metal ion (Table 2), reflecting its greater ability to accept charge. This higher tendency for Cu^{2+} to capture electrons may be reflected in its greater ability to stabilise its metal diketonate complexes when compared to other transition metal complexes.

Furthermore, in aqueous solution these borderline dipositive metal ions considered are six-coordinate[24] with the exception of copper, which is four-coordinate and consequently, in aqueous solution, has a small radius (0.57 Å) when compared with cobalt (0.72 Å) and nickel (0.69 Å). Since hardness values are reduced by solvent effects, it can be expected that hexaaqua metal ions such as cobalt(II) and nickel(II) will show a more decreased hardness than a tetraaqua species such as copper(II). Thus Cu^{2+}(aq) might be regarded as a pseudo-hard acid when compared with Co^{2+}(aq) and Ni^{2+}(aq). The extra-hardness of copper may arise because it has a tightly packed coordination sphere.

In addition to the expected effects of ionic charge and size, the influence of d electrons may be considered in the apparent extra-low borderline behaviour of Co^{2+}. That the d subshell is very important in promoting soft behavior has been emphasised by Ahrland.[25] The role of the d electrons in chemical bonding is usually attributed to polarisation in the field of the ligands, and it is interesting to point out that this is also a polarisability effect.

From these results, it seems difficult to establish a universal order of bond tendencies and absolute hardness which is useful simultaneously in the gas phase and in aqueous solution. The approach to quantifying hardness by η here further means that this single absolute physical quantity would not be an absolute measure of hardness in aqueous solution.

Although the concept of electronegativity is almost as old as

chemistry itself,[26] at the moment there is not an equivalent HSAB principle which considers χ instead of η when thinking about reactivity tendencies in chelate compounds. When considering the stability of diketonate metal complexes in aqueous solution, the χ scale (Table 2) might give a better interpretation of Fig. 1 than η scales. Perhaps the hardness parameter should be properly supplemented by a new parameter related to absolute electronegativity for a better prediction of correct directionality of coordination reactions in aqueous solution. We are working on this possibility at present.

The overall goal of this work was to predict reactivities in terms of stability constants. In this sense previous equations[27] proposed for the prediction of the stability constants of complex formation were able to correlate available data. A real test of previous equations is their ability to predict data that were not available at the time that the equations were published and this has been done. Graphical analysis (i.e. Fig. 1) has been a clear way to obtain an intuitive feel for the behavior of these compounds. The fact that the lines converge to a log β value rather close to zero indicates that, for structurally similar ligands with known pK, stability and equilibrium constants of their 1:1 metal complexes may be predicted. Furthermore, considering a hypothetical metal ion or oxo-metal ion for which I and A parameters are known, a correlative dependence similar to the lines in Fig. 1 might be, approximately, interpolated.

A possible limitation of this is that while we are well supplied with I values for many systems, there is still a great shortage of A values. It is hoped that new experimental methods will make these available.

Experimental

Pentane-2,4-dione, hexane-2,4-dione, heptane-3,5-dione, 2,6-dimethylheptane-3,5-dione, 1-(2-thienyl)butane-1,3-dione and 1,1,1-trifluoropentane-2,4-dione were obtained from Kodak; octane-2,4-dione and nonane-2,4-dione were purchased from Ventron; 2,2,6,6-tetramethylheptane-3,5-dione was obtained from Sigma; 6-methylheptane-2,4-dione and 2-acetylcyclohexanone were purchased from Fluka; and 2-acetylcyclopentanone was obtained from Aldrich, all of them reagent grade. All were purified by distillation under reduced pressure, except 1-(2-thienyl)butane-1,3-dione which was purified by recrystallisation. Stock solutions were standardised by titration with standard sodium hydroxide.

Stock solutions of $Ni(ClO_4)_2 \cdot 6H_2O$ (Aldrich), $Cu(NO_3)_2 \cdot 3H_2O$ (B.D.H.), $Co(ClO_4)_2 \cdot 6H_2O$ (Aldrich), $Cr(NO_3)_3 \cdot 9H_2O$ (Aldrich), $Fe(NO_3)_3 \cdot 9H_2O$ (Merck), $VOSO_4 \cdot 3H_2O$ (Aldrich), and $UO_2(NO_3)_2 \cdot 6H_2O$ (AnalaR) were standardised using recognised procedures.[7]

Unless otherwise indicated, all other materials were of reagent grade (Merck), and were used without further purification.

Potentiometric and pH measurements were made with a Crison 501 pH-meter equipped with an Ingold combination glass-and-reference electrode. Spectra and absorption data were recorded on a Spectronic 1201 UV–Vis spectrophotometer coupled with a graphic recorder BBC SE 790.

Reactions were studied in aqueous perchloric acid media at 25 °C. The ionic strength of reactant solutions was adjusted to 0.5 mol dm^{-3} using $NaClO_4 \cdot H_2O$.

Acknowledgements

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