Ligands Containing Elements of Group VIB. Part VI.[1] Transition Metal Complexes of Some Alkyl- and Aryl-thioacetic and -selenoacetic Acids

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Formation constants for complexes of some alkyl- and aryl-thioacetic and selenoacetic acids with divalent transition metal ions have been measured at 25° and $I = 0{\cdot}10$M (KNO_3) using a method based on competing equilibria between silver and the metal ions for co-ordination to the ligands. A computerized minimization procedure is described. Complexes formed are of low stability but follow the general pattern of formation constants: alkyl > aryl; thio- > seleno- and $Cu^{2+} > Co^{2+}$, $\sim Mn^{2+}$, $\sim Zn^{2+} > Ni^{2+}$, with Cd^{2+} showing variable class (a)–(b) character.

SUBSTITUTED thioacetic and selenoacetic acids form comparatively stable complexes with silver ions in aqueous solution. Earlier papers in this series reported the results of a study of stability constants and enthalpy changes accompanying the formation of mono-, bis- and protonated silver complexes.[1,2] These results have been interpreted in terms of the relative affinities of sulphur(II) and selenium(II) donors for silver ions, and the electronic effects of the various substituent groups in the ligands. Silver(I) is known to show marked class (b) character[3] and, therefore, is expected to form stable complexes with ligands containing heavy donor atoms. Divalent metals of the first transition series, however, are 'harder' or more class (a) in character and so would be expected to show a comparatively smaller affinity for ligands with heavy donor atoms than for those from the first period.

There are few experimental results in this field. Thioacetic and selenoacetic acid complexes of divalent transition metal ions tend to be of low stability. Such results as there are have been measured by following the proton displacement caused by complex formation between the metal ions and substituted acetic acids, *i.e.* the Bjerrum method.[4,5] However this proton displacement will take place from the carboxy-group and will be comparatively insensitive to complex formation between the metal ion and sulphur or selenium atoms which do not protonate readily. We have therefore derived a procedure for studying these weak complexes which is far more sensitive to co-ordination through the heavy donor atom. Equilibria between the ligands and silver ions in competition with divalent metal ions have been followed by means of a silver–silver chloride indicator electrode, using a mercury–mercurous sulphate reference electrode. Knowing the stability constants of the various silver complexes, those of the divalent ion complexes can be found by a calculation similar to the Bjerrum technique for proton-displacement reactions. Silver co-ordinates predominately through the heavy donor atom, and, since the potential of silver–silver chloride indicator electrode can be measured much more precisely than that of a glass electrode, stability constants calculated for weak transition metal complexes should be more reliable.

The constants so calculated will be macro-constants, with components from co-ordination through both the heavy donor atom and the acetate groups of the ligands. Co-ordination through the oxygen of the acetate group would be expected to compare reasonably closely with co-ordination of the proton (*i.e.* p*K* values). Hence a comparison of measured stability constants with p*K* values should give an indication of the variations in co-ordination between the heavy donor atom and transition metal ions.

EXPERIMENTAL

Ligands were prepared as described previously.[6] Metal-ion solutions were prepared from AnalaR reagents and standardized with e.d.t.a.

Metal complex formation constants were measured using apparatus described previously,[6] with the addition of a glass electrode to monitor the pH continuously throughout a titration. The titration vessel contained a mixture of silver ions (*ca.* 10^{-3}M) and divalent metal ions (*ca.* 10^{-2}M) with the ionic strength of the solution adjusted to 0·1M with KNO_3. Concentrated ligand solution was added from a burette and the potentials of the silver–silver chloride and glass electrodes measured relative to a saturated mercurous sulphate electrode. The indicator electrodes was calibrated in terms of silver and hydrogen ion concentrations respectively.

Earlier work in this series was carried out in an acetate buffer solution since silver was the only metal ion studied and silver–acetate complexes are very weak. Divalent metal ions would co-ordinate more strongly with the acetate group making use of an acetate buffer unwise. The silver complex formation constants were therefore redetermined in a nitrate solution in which the pH was kept constant by the addition of free acid or base as required. It was found that the silver complex formation constants in a nitrate background agreed with those in an acetate buffer of the same pH to within 0·04 log units. In addition the calculated constants were virtually independent of pH over the range of 5·7—6·1. Below a pH of 5·7 a correction for the presence of the protonated ligand, HL, was required and above 6·1 hydrolysis of the

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[1] Part V, D. S. Barnes, G. J. Ford, L. D. Pettit, and C. Sherrington, *J. Chem. Soc.* (*A*), 1971, 2883.

[2] D. S. Barnes, P. G. Laye, and L. D. Pettit, *J. Chem. Soc.* (*A*), 1969, 2073.

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[4] K. Suzuki, C. Karaki, S. Mori, and K. Yamasaki, *J. Inorg. Nuclear Chem.*, 1968, **30**, 167.

[5] G. J. Ford, L. D. Pettit, and C. Sherrington, *J. Inorg. Nuclear Chem.*, 1971, **33**, 4119.

[6] L. D. Pettit and C. Sherrington, *J. Chem. Soc.* (*A*), 1968, 3078 and references therein.

silver was found to be significant. In the presence of divalent metal ions considerably lower pH values were frequently required to prevent hydrolysis. During such titrations the pH was measured accurately for each data point so that necessary corrections could be applied. The pH ranges used for various metal ions were as follows: cadmium, 5·7—6·0; zinc, 5·7—6·0; manganese, 5·7—6·0; nickel, 5·4—5·6; cobalt(II), 4·2—4·4; copper(II), 4·8—4·9.

The presence of significant hydrolysis would have become immediately apparent from both pH and pAg measurements.

Calculation Procedure.—In solutions in which the pH is more than 1 unit above the pK unit value of the ligand HL, the only protonated species expected is the monosilver complex, AgHL. Under such conditions, and assuming no hydrolysis, the following relationships were assumed to describe the system:

$$C_{\mathrm{Ag}} = [\mathrm{Ag}] + [\mathrm{AgL}] + [\mathrm{AgHL}] + [\mathrm{AgL_2}] + 2[\mathrm{Ag_2L}] \quad (1)$$

$$C_{\mathrm{M}} = [\mathrm{M}] + [\mathrm{ML}] \quad (2)$$

$$C_{\mathrm{L}} = [\mathrm{L}] + [\mathrm{HL}] + [\mathrm{AgL}] + [\mathrm{AgHL}] + 2[\mathrm{AgL_2}] + [\mathrm{Ag_2L}] + [\mathrm{ML}] \quad (3)$$

where C_{Ag}, C_{M}, and C_{L} are the total concentrations of silver, divalent metal ion, and ligand respectively. Since all the relevant silver complex formation constants in an acetate buffer had been determined earlier it was possible, by assuming these values, to calculate a value for K_{ML} for each point on the titration curve. In practice this value was found to be sensibly constant throughout a titration suggesting that omission of species such as $\mathrm{ML_2}$ and MHL was justified. Further, the value calculated for K_{ML} was insensitive over the experimental range used to small errors in the values selected $\beta_{\mathrm{Ag_2L}}$ and $\beta_{\mathrm{AgL_2}}$ since these were always minority species. Precise values for K_{AgL} and K_{ML} were then calculated by means of the following computerized minimization procedure. In all cases it was found that the final values calculated for K_{AgL}, applicable to a background of 0·1M-$\mathrm{KNO_3}$, were in agreement to within 0·01 log units of values calculated from titrations in the presence of silver alone with the same background. A sample set of data for one of the weaker complexes, the silver–cobalt–*m*-methoxyphenylthioacetic acid system, is shown in Table 1, to demonstrate the range of $\bar{n}$ and K_{CoL} values, assuming fixed values for formation constants of the silver complexes.

TABLE 1

Values calculated for K_{CoL}, where L is *m*-$\mathrm{MeOC_6H_4SCH_2CO_2^-}$, assuming the values $\beta_{\mathrm{AgL}} = 506{\cdot}1$ l mol^{-1}, $\beta_{\mathrm{AgHL}} = 123{\cdot}0$ (l mol^{-1})^2 and $\beta_{\mathrm{AgH_2L}} = 15{,}000$ (l mol^{-1})^3

a) Vol. ligand soln. added/ml	1·0	1·2	1·4	1·6	1·8	2·0	2·2	2·4	2·6	2·8	3·0	3·2	3·4	3·6	3·8	4·0	4·2	4·4	4·6	4·8	5·0
b) $\bar{n}/10^{-3}$	0·81	0·97	1·13	1·29	1·45	1·60	1·76	1·92	2·08	2·24	2·39	2·53	2·70	2·85	2·99	3·14	3·29	3·44	3·59	3·75	3·89
c) K_{ML}/(l mol^{-1})	4·99	4·95	4·65	4·83	4·76	4·84	5·04	4·77	4·77	4·63	4·72	5·00	4·72	4·84	5·12	5·12	5·23	5·25	5·26	5·17	5·30

Minimization Procedure.—The value of C_{L} may be calculated from equation (3) using the same set of known values as before, but regarding K_{ML} and K_{AgL} as adjustable parameters. These parameters are then varied so as to optimize the agreement between the calculated value of C_{L}, and the experimentally known value, *i.e.* the R-factor (4) is minimized. R is a non-linear function of the parameters and cannot be differentiated partially

$$R = \sum^{\mathrm{expts}} (C_{\mathrm{L}}^{\mathrm{obs}} - C_{\mathrm{L}}^{\mathrm{calc}})^2 \quad (4)$$

with respect to them. The function must therefore be minimized either by a method that performs the differentiation numerically, *e.g.* SCOGS,[7] or by a 'direct search' method such as 'pit mapping'[8] or 'Powell 64'.[1]

We have developed a new method which is usually more efficient than those referred to above. It was a variant of the Davidon–Fletcher–Powell method[9] in which both the gradient vector **g** and the inverse Hessian $\mathbf{H}^{-1}$ are built up numerically ($g_i = \partial R/\partial x_i$, $H_{ij} = \partial^2 R/\partial x_i \partial x_j$, x_i and x_j are the adjustable parameters). It is therefore superior to the SCOGS type of method which calculates the Jacobian, **J**, numerically since **H** is well approximated by $2\tilde{\mathbf{J}}\mathbf{J}$ only when the function R is linear in the parameters, but it is equivalent to the assumption (used in LETAGROP[8]) that the 'pit' can be represented by a general quadratic function of the parameters. The method is embodied in the ALGOL procedure Dapodmin,[10] details of which, in its implementation for force-constant computations, have been given elsewhere.[11] A further useful feature of the method is that the standard errors in the computed parameters can be obtained by making the assumption that $\mathbf{H} \simeq 2\tilde{\mathbf{J}}\mathbf{J}$ at the solution.

Iteration on only two parameters (K_{ML} and K_{AgL}) does not take full advantage of the minimization procedure described. The procedure was therefore used to refine the constants calculated from the data for some silver-substituted arsine complexes.[12] These ligands were dibasic acids, $\mathrm{H_2L}$, of general formula $\mathrm{R{\cdot}C_6H_4{\cdot}As(CH_2CO_2H)_2}$, and formed three silver complexes under the conditions used, *i.e.* AgL, AgHL, and $\mathrm{AgH_2L}$. Refined constants are given in Table 2 together with published values calculated by a graphical method. The standard deviations given in Table 2 give the relative precision of the constants but may be optimistic in absolute terms.

RESULTS AND DISCUSSION

Calculated formation constants are shown in Table 3 together with those previously reported for the silver complexes in acetate media. The standard deviations (σ-values) refer to the spread throughout duplicate titrations under identical experimental conditions and therefore reflect the precision of the measurements rather than their absolute values.

Of the metal ions studied copper(II), apart from silver, forms the most stable complexes with all the ligands, complexes with alkyl groups on the donor atoms being more stable than those with aryl substituents as would be expected if the donor to metal bonds are essentially

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[10] S. A. Lill, *Computer J.*, 1970, **13**, 111.

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[12] L. D. Pettit and A. Royston, *J. Chem. Soc.* (*A*), 1969, 1570.

σ-donor in character. However the difference in stability of the aryl and alkyl substituted divalent metal ion complexes is markedly less than that of the silver complexes; hence the precision with which the formation constants of alkyl substituted transition metal complexes could be measured is less than with the aryl analogues. In all cases studied, the copper complexes of ligands containing selenium donor atoms are weaker than the sulphur analogues. With cadmium this trend is less noticeable and it is reversed in the case of silver, a markedly class (b) acceptor. *o*-Methoxy-substituted ligands, however, co-ordinated more strongly with copper than do their unsubstituted analogues, showing that co-ordination though the methoxy-oxygen is important. As expected, this enhancement is far less significant with silver.

TABLE 2

Refined silver complex formation constants for substituted bis(carboxymethyl)phenylarsines, $R\cdot C_6H_4\cdot As(CH_2CO_2H)_2$. σ-Values are given in parentheses

	Refined values			Original values (ref. 12)		
R	log K_{AgL}	log K_{AgHL}	log K_{AgH_2L}	log K_{AgL}	log K_{AgHL}	log K_{AgH_2L}
H	6·13(1)	5·126(2)	4·643(2)	6·29	5·16	4·65
o-OMe	6·14(3)	4·67(2)	4·540(10)	5·90	4·83	4·35
m-OMe	6·20(2)	4·804(8)	4·556(2)	6·19	5·12	4·54
p-OMe	6·36(1)	5·495(5)	4·759(6)	6·45	5·46	4·89
o-Me	5·93(2)	4·981(2)	4·412(2)	6·00	4·95	4·35
m-Me	6·06(2)	4·967(7)	4·403(3)	6·30	4·96	4·44
p-Me	6·44(3)	5·577(4)	4·827(3)	6·44	5·43	4·84
o-Cl	5·20(10)	4·13(1)	4·045(5)	5·34	4·75	4·10
p-Cl	5·96(2)	4·958(5)	4·466(2)	6·11	4·88	4·40

TABLE 3

Formation constants of complexes of some thio- and seleno-acetic acids at 25° and I = 0·10M (KNO_3) (σ-values in parentheses)

Ligand $X\cdot CH_2CO_2^-$	K_{ML} (l mol^{-1})								
	Ag^+		Cd^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}	Zn^{2+}	H^+
X =									
C_6H_5S	676	589 [a]	4·7(2)	27(1)	2·0(2)	5·8(4)	5·2(4)	2·1(1)	2400 [b]
C_6H_5Se	4800	4210	4·8(2)	19(1)	n.m. [c]	4·3(1)	2·1(2)	4·0(5)	5620
o-$MeOC_6H_4S$	895	1050	7·2(3)	69(2)	0·8(2)	5·5(2)	3·2(6)	9·9(6)	2400
o-$MeOC_6H_4Se$	520	5250	6·7(4)	45(3)	n.m.	4·5(3)	3·1(2)	5·1(2)	5750
m-$MeOC_6H_4S$	506	443	6·1(2)	45(3)	1·7(3)	5·0(3)	3·9(4)	4·8(2)	2450
$CH_3\cdot(CH_2)_3S$	10,380	8360	8·1(9)	90(2)					5500
$CH_3\cdot(CH_2)_3Se$	44,570	37,670	5·0(8)	90(6)					8510
$CH_2{:}CH(CH_2)_2S$	50,350	58,480	3·2(3)	135(6)					5250
$CH_2{:}CH(CH_2)_2Se$	82,790	1,4550	5·0(9)	105(11)					7590

[a] Values determined in an acetate buffer, I = 0·2M, refs. 1, 6. [b] Ref. 1 and L. D. Pettit, A. Royston, C. Sherrington, and R. J. Whewell, *J. Chem. Soc.*, (*B*), 1968, 588. [c] n.m., Not measurable.

Since the complexes are all very weak, more detailed analysis of the results would not be meaningful. However one surprising result stands out clearly; without exception the nickel complexes are all very weak indeed and are not in line with the Irving–Williams order of stabilities. Suzuki and Yamasaki also reported [13] very weak nickel complexes with phenylthioacetic acid (*i.e.* K_{NiL} *ca.* 5 l mol^{-1}). There is no immediate explanation for this low stability. The possibility that Ni^{2+} ions affect the potential of the silver halide electrode was ruled out since the value for E_0 was virtually independent of the presence of nickel ions in the ionic background. Sandell has studied the nickel-ethylthioacetic acid system potentiometrically [14] and obtained a value of K_{NiL} = 11·0 l mol^{-1} (pH titration) compared to values of 365 for K_{CuL} and 18·7 for K_{CdL} (Cu and Cd electrode titrations).

[2/692 *Received, 24th March,* 1972]

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