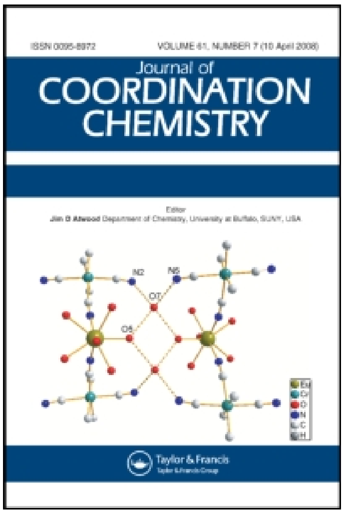

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A POTENTIOMETRIC AND CALORIMETRIC STUDY OF THE THERMODYNAMICS OF FORMATION OF SOME OF THE COMPLEXES OF THE d^{10} METAL IONS SILVER(I), MERCURY(II), AND CADMIUM(II) WITH THIODIGLYCOL, THIOUREA, AND THE SULPHITE ION

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The standard free energy, enthalpy, and entropy changes of complex formation of the d^{10} metal ions Ag(I), Hg(II), and Cd(II) with the *S*-donor-atom ligands thiodiglycol, thiourea, and sulphite were investigated at 298.15 ± 0.05 K. The free-energy changes ΔG_i° were calculated from stability constants β_i, which were determined by silver- and mercury-electrode potentiometry, if suitable literature data were not available. Enthalpy changes ΔH_i° were measured with a titration calorimeter, and entropy changes ΔS_i° were calculated from the relation $\Delta G_i^\circ = \Delta H_i^\circ - T\Delta S_i^\circ$. The standard state, denoted by the superscript ° in ΔG°, ΔH°, and $T\Delta S^\circ$, refers, in most cases, to a hypothetical 1 M solution in which the ionic strength, μ, is 0.5 M.

It is demonstrated that a large proportion of the extra stabilization of the HgL_n complexes compared with the corresponding AgL_n complexes is a result of a more favourable entropy contribution. The entropies of complexation are interpreted in terms of the Powell, Latimer, and Cobble theory, and an explanation is advanced for the favouring of complexes of co-ordination number two for Ag(I) and Hg(II) complexes.

INTRODUCTION

In a review article published recently,[1] Nancollas pointed out that, in order to obtain a better understanding of complex formation reactions, more data on the thermodynamics of complex formation reactions were needed. In the same year, Christensen and Izatt published a compilation[2] of values of ΔH, log k, and ΔS covering the period up to 1969.

An investigation was undertaken of the standard free energies, enthalpies, and entropies of complex formation of the d^{10} metal ions Ag(I), Hg(II), and Cd(II) with the monodentate ligands thiodiglycol, thiourea, and sulphite in an attempt to supplement literature data for complexes involving ligands having an *S* donor atom, and as part of a general investigation into the thermodynamics of the complex formation of transition metal ions. The free-energy changes ΔG_i° were calculated from stability constants β_i, which were determined by silver- and mercury-electrode potentiometry where suitable literature data were not available. Enthalpy changes ΔH_i° were measured with a titration calorimeter, and entropy changes ΔS_i°, or the entropy contribution $T\Delta S_i^\circ$ to the free energy of complex formation, was obtained from the relation

$$\Delta G_i^\circ = \Delta H_i^\circ - T\Delta S_i^\circ \qquad (1)$$

The standard state, denoted by the superscript ° in ΔG°, ΔH°, and $T\Delta S^\circ$, refers, in most cases, to a hypothetical 1 M solution in which the ionic strength μ is 0.5 M.

EXPERIMENTAL

Most of the measurements in this study were made at 298.15 ± 0.05 K in an aqueous medium of ionic strength $\mu = 0.50$ M with, in most cases, sodium perchlorate as background electrolyte. For the Hg^{2+} + thiourea system, in which a high concentration of acid was needed to stabilize the complexes, perchloric acid was used to make up the ionic strength to 0.5 M. For Ag^+ + thiourea, the ionic strength was adjusted to 0.02 M with $NaClO_4$.

Materials

Stock solutions of $AgNO_3$ were prepared from A.R.-grade $AgNO_3$, and were standardized potentiometrically against standard NaCl solutions with the use of a silver electrode. Stock solutions of $Hg(ClO_4)_2$ were made up by dissolving an excess of BDH mercuric oxide in MERCK G.R. perchloric acid that had been standardized against recrystallized borax. The solution was analysed by potentiometric titration against standard NaCl solution with the use of a mercury electrode so that the end point at $HgCl_2$ could be detected. More mercuric oxide dissolved than could be accounted for on the basis of the perchloric acid concentration, which showed that an appreciable amount of mercury went into solution as $Hg(OH)ClO_4$. A calculated quantity of perchloric acid was added to convert the solution entirely to $Hg(ClO_4)_2$. Stock solutions of $Cd(ClO_4)_2$ were prepared by dissolving MERCK anhydrous cadmium oxide in perchloric acid, and were standardized by EDTA titration.[3] Thiodiglycol G.R. and thiourea G.R. were purchased from E. MERCK, and the former was analysed by bromometric titration.[4] Sulphite stock solutions were made up from the A.R. grade sodium salt, and were analysed by a literature method.[5]

Potentiometric Apparatus and Procedure

Stability constants involving Ag were determined with the use of an electrochemical cell consisting of a silver wire indicating electrode and silver chloride reference electrode, together with a salt bridge to prevent contamination of the reaction solution with Cl^- ions. The liquid junctions between the reference electrode and the salt bridge, and between the salt bridge and the solution, were made using the glass outer tube together with sintered glass discs taken from a standard INGOLD reference electrode. Junction potentials were minimized by the use of 0.5 M sodium perchlorate in the salt bridge, and by making up of the ionic strength of the solution in the reference electrode itself to 0.5 M with $NaClO_4$. Thus, a typical reference electrode consisted of an INGOLD silver wire coated with silver chloride dipping into a reference solution which was 0.01 M NaCl + 0.49 M $NaClO_4$. A drop of dilute $AgClO_4$ solution was added so that the reference solution would be saturated with AgCl. Presaturated nitrogen was bubbled through the cell to exclude oxygen and carbon dioxide, and the cell potential was measured with the use of a RADIOMETER PHM 64 research pH-meter.

Stability constants involving Hg were determined with a J-type mercury-indicating electrode described in the literature.[6] The J-tube was siliconed to prevent solution from creeping down the sides of the mercury pool. Contact on the long arm of the J-tube was made with a short length of platinum wire sealed into a glass tube so that the whole length of wire was immersed in the mercury. The remainder of the cell was the same as that described for the Ag measurements.

Calorimetric Apparatus and Procedure

The enthalpy changes were determined with the use of a titration calorimeter, which has been described previously.[7] The way in which the calorimetric data are corrected for heat exchange, difference in temperature between titrant and titrate, and for 'non-chemical' heat effects has been described by Eatough *et al.*[8] The calorimeter was calibrated using an LKB calibration heater in a constant current circuit. The overall accuracy of the calorimeter and the corrections applied were checked by measuring the standard enthalpy changes of two well documented reactions.[7]

Calculations

Stability constants were calculated from potentiometric data with the use of the ETITR form of the LETAGROP VRID suite of programmes.[9] These calculations were checked with the use of the MINIQUAD programme of Sabatini *et al.*[10] Enthalpy changes of complex formation were calculated from the calorimetric data, and known stability constants with the use of the KALLE form[11] of LETAGROP VRID.

Corrections were made for any side reactions known to be taking place in the experiment, e.g., hydrolysis of the metal ions and ligand protonation. Hydrolysis of the metal ions occurs because, in the case of SO_3^{2-}, the ligand has sufficient basicity to raise the pH of the solution significantly. For Ag^+, the metal-hydroxide stability constant of $\log \beta_1 = 3.02$[12] is relatively low, leading to negligible corrections for metal hydrolysis. Values of the hydroxylation constants and enthalpies of hydroxylation of Cd and Hg, together with the value of the ion product of water and the heat of combination of H^+ and OH^- used in this investigation are shown in Table I.

The error introduced by the fact that the data for Cd^{2+} and the enthalpies of hydroxylation of Hg^{2+}, given in Table I, were determined at an ionic strength other than 0.5 M, is second order and can be neglected. It has been shown[14] that, at ionic strength

TABLE I

Metal-hydroxide stability constants and enthalpies for Cd^{2+} and Hg^{2+}, together with the ion product of water, and the enthalpy of combination of H^+ and OH^-, used in this study

Reaction	log β	μ/M	Reference	$\Delta H°$/kJ mol^{-1}	μ/M	Reference
$Cd^{2+} + OH^- \rightleftharpoons CdOH^+$	6.08	0	13	−1.67	3	16
$Hg^{2+} + OH^- \rightleftharpoons Hg(OH)^+$	10.04	0.5	14	−24	3	17
$Hg^{2+} + 2OH^- \rightleftharpoons Hg(OH)_2$	21.18	0.5	14	−68	3	17
$H^+ + OH^- \rightleftharpoons H_2O$	13.74	0.5	15	−56.90	0.5	18

and concentration conditions similar to those used in this work, no polynuclear mercury hydroxide species are formed.

The formation of mercurous ions according to the reaction $Hg^{2+} + Hg_{(l)} \rightleftharpoons Hg_2^{2+}$ was taken into account by use of a reported value of 130 for the equilibrium constant of this reaction.[19]

MEASUREMENTS AND RESULTS

In Table II the experimental data for the potentiometric titrations are given, and in Table III the data obtained from the calorimetric titrations are given. Any special features encountered with the various systems will be discussed separately.

TABLE II

Potentiometric measurements. Experimental data for the calculation of stability constants. $E°_{\mathrm{cell}}$ comes from the Nernst equation $E_{\mathrm{cell}} = E°_{\mathrm{cell}} + \frac{RT}{nF}\ln[\mathrm{M}^{n+}]$, the subscript (o) refers to the titrate and (T) refers to the titrant. The proton concentration [H] refers to the total excess proton concentration in solution. The concentrations of background electrolyte are omitted for simplicity. The volume/e.m.f. data are given as pairs ($V_{\mathrm{T}}, E_{\mathrm{cell}}$), separated by semi-colons, and are given in units of cm^3 and mV respectively.

(i) System: Ag^+ + thiodiglycol
$E°_{\mathrm{cell}} = 752$ mV. $[\mathrm{Td}]_{\mathrm{o}} = 0$ M, $[\mathrm{Ag}]_{\mathrm{o}} = 0.0413$ M, $[\mathrm{Td}]_{\mathrm{T}} = 0.9726$ M, $[\mathrm{Ag}]_{\mathrm{T}} = 0$ M. Vo = 48.00 cm^3.
2.00, 619; 2.50, 606; 3.00, 588; 3.50, 572; 4.00, 555; 4.50, 536; 5.00, 515; 5.50, 502; 6.00, 490; 6.50, 480; 7.00, 471; 7.50, 463; 8.00, 456; 9.00, 443; 10.00, 432; 12.00, 416; 15.00, 396; 20.00, 374; 25.00, 357; 30.00, 343; 35.00, 334; 40.00, 325.

(ii) System: Hg^{2+} + thiodiglycol
$E°_{\mathrm{cell}} = 879.33$ mV. $[\mathrm{Td}]_{\mathrm{o}} = 0.0121$ M, $[\mathrm{H}]_{\mathrm{o}} = 0.0100$ M, $[\mathrm{Hg}]_{\mathrm{o}} = 0$ M, $[\mathrm{Td}]_{\mathrm{T}} = 0$ M, $[\mathrm{H}]_{\mathrm{o}} = 0.0100$ M, $[\mathrm{Hg}]_{\mathrm{T}} = 0.0492$ M. Vo = 31.00 cm^3.
0.25, 571.0; 0.50, 590.8; 0.75, 600.5; 1.00, 607.6; 1.25, 613.6; 1.50, 619.1; 1.75, 624.6; 2.00, 629.9; 2.25, 635.5; 2.50, 641.5; 2.75, 648.4; 3.00, 656.1; 3.25, 665.6; 3.50, 677.1; 3.75, 689.9; 4.00, 700.7.

(iii) System: Ag^+ + thiourea
$E°_{\mathrm{cell}} = 772.09$ mV. $[\mathrm{Tu}]_{\mathrm{o}} = 0$ M, $[\mathrm{Ag}]_{\mathrm{o}} = 4.00 \times 10^{-3}$ M, $[\mathrm{Tu}]_{\mathrm{T}} = 0.2003$ M, $[\mathrm{Ag}]_{\mathrm{T}} = 0$ M. Vo = 48.00 cm^3.
0.10, 629; 0.30, 620; 0.50, 611; 0.80, 591; 1.00, 571; 1.20, 545; 1.30, 528; 1.40, 504; 1.50, 462; 1.60, 411; 1.70. 381; 1.80, 361; 2.00, 335; 2.30, 307; 2.60, 287; 3.00, 265; 3.60. 240; 4.40, 216; 5.20, 198; 6.00, 183; 8.00, 156; 10.00, 137; 14.00, 111; 1.80, 90; 22.00, 77; 30.00, 56.

(iv) System: Hg^{2+} + thiourea
$E°_{\mathrm{cell}} = 492.20$ mV. $[\mathrm{Tu}]_{\mathrm{o}} = 0$ M, $[\mathrm{H}]_{\mathrm{o}} = 0.490$ M, $[\mathrm{Hg}]_{\mathrm{o}} = 9.46 \times 10^{-3}$ M, $[\mathrm{Tu}]_{\mathrm{T}} = 0.1013$ M, $[\mathrm{H}]_{\mathrm{T}} = 0.500$ M, $[\mathrm{Hg}]_{\mathrm{T}} = 0$ M. Vo = 37.00 cm^3.
0.50, 368.5; 1.00, 367.1; 2.00, 363.6; 3.00, 359.6; 4.00, 354.9; 5.00, 347.5; 6.00, 335.8; 9.00, −48.2; 10.00, −68.4; 11.00, −85.8; 12.00, −100.0; 13.00, −112.5; 14.00, −122.8; 15.00, −131.8; 16.00, −139.7; 17.00, −146.8; 18.00, −152.4; 19.00, −158.0; 20.00, −162.6; 25.00, −181.4; 35.00, −203.3.

$E°_{\mathrm{cell}} = 492.10$ mV. $[\mathrm{Tu}]_{\mathrm{o}} = 0$ M, $[\mathrm{H}]_{\mathrm{o}} = 0.490$ M, $[\mathrm{Hg}]_{\mathrm{o}} = 9.46 \times 10^{-3}$ M, $[\mathrm{Tu}]_{\mathrm{T}} = 0.1013$ M, $[\mathrm{H}]_{\mathrm{T}} = 0.500$ M, $[\mathrm{Hg}]_{\mathrm{T}} = 0$ M. Vo = 35 cm^3.
1.00, 361.8; 2.00, 356.8; 3.00, 349.3; 4.00, 336.7; 8.00, −90.2; 9.00, −108.0; 10.00, −121.4; 11.00, −132.8; 12.00, −142.2; 13.00, −150.2; 14.00, −156.9; 15.00, −163.1; 16.00, −168.1; 17.00, −172.9; 18.02, −177.2; 19.00, −181.0; 20.00, −184.4; 25.00, −198.6; 35.06, −216.1.

(v) System: Hg^{2+} + sulphite
$E°_{\mathrm{cell}} = 489.86$ mV. $[\mathrm{SO_3}]_{\mathrm{o}} = 0.02663$ M, $[\mathrm{H}]_{\mathrm{o}} = 0$ M, $[\mathrm{Hg}]_{\mathrm{o}} = 0$ M, $[\mathrm{SO_3}]_{\mathrm{T}} = 0$ M, $[\mathrm{H}]_{\mathrm{T}} = 0$ M, $[\mathrm{Hg}]_{\mathrm{T}} = 0.0492$ M. Vo = 30.00 cm^3.
0.50, −197.7; 1.00, −186.4; 1.50, −179.3; 2.00, −172.9; 2.50, −167.6; 3.00, −162.6; 3.50, −157.6; 4.50, −147.7; 5.00, −142.1; 5.50, −135.6; 6.00, −128.3; 6.50, −119.2; 7.00, −107.1; 7.50, −85.4.

TABLE III

Calorimetric measurements. Experimental data for the calculation of enthalpy changes. The subscript (o) refers to the titrate and (T) refers to the titrant. The proton concentration [H] refers to the total excess proton concentration in solution. The concentrations of background electrolyte are omitted for simplicity. The data for volume per incremental heat liberated are given as pairs (V_T, h) separated by semi-colons, and are given in units of cm^3 and J respectively.

(i) System: Ag^+ + thiodiglycol.
$[\mathrm{Ag}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Td}]_\mathrm{o} = 0$ M, $[\mathrm{Ag}]_\mathrm{T} = 0$ M, $[\mathrm{Td}]_\mathrm{T} = 1.016$ M. Vo = 95.00 cm^3.
0.26, 8.23; 0.56, 8.96; 0.86, 8.20; 1.16, 7.42; 1.46, 6.42; 1.76, 4.95; 2.06, 3.74; 2.36, 2.79; 2.66, 2.10; 2.96, 1.51; 3.26, 1.36; 3.56, 1.10; 3.86, 0.94; 4.16, 0.84; 4.46, 0.79; 4.76, 0.74.

$[\mathrm{Ag}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Td}]_\mathrm{o} = 0$ M, $[\mathrm{Ag}]_\mathrm{T} = 0$ M, $[\mathrm{Td}]_\mathrm{T} = 1.016$ M. Vo = 95.00 cm^3.
0.20, 6.38; 0.45, 7.41; 0.70, 7.42; 0.95, 6.67; 1.20, 5.97; 1.45, 5.09; 1.69, 4.31; 1.94, 3.41; 2.19, 2.61; 2.44, 2.05; 2.69, 1.77; 2.93, 1.28; 3.18, 1.12; 3.43, 0.91; 3.68, 0.97; 3.93, 0.75; 4.17, 0.59; 4.42, 0.70; 4.67, 0.60; 4.91, 0.54.

$[\mathrm{Ag}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Td}]_\mathrm{o} = 0$ M, $[\mathrm{Ag}]_\mathrm{T} = 0$ M, $[\mathrm{Td}]_\mathrm{T} = 1.016$ M, Vo = 95.00 cm^3.
0.21, 6.68; 0.46, 7.55; 0.71, 7.25; 0.95, 6.67; 1.20, 5.87; 1.45, 5.11; 1.70, 4.45; 1.94, 3.29; 2.19, 2.71; 2.44, 2.07; 2.69, 1.59; 2.93, 1.39; 3.18, 1.06; 3.43, 0.96; 3.68, 0.86; 3.92, 0.92.

(ii) System: Hg^{2+} + thiodiglycol
$[\mathrm{H}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Hg}]_\mathrm{o} = 0.00984$ M, $[\mathrm{Td}]_\mathrm{o} = 0$ M, $[\mathrm{H}]_\mathrm{T} = 0.0100$ M, $[\mathrm{Hg}]_\mathrm{T} = 0$ M, $[\mathrm{Td}]_\mathrm{T} = 1.016$ M.
Vo = 95.00 cm^3.
0.26, 8.49; 0.56, 10.16; 0.86, 9.63; 1.16, 10.35; 1.46, 10.41; 1.76, 10.09; 2.06, 3.65; 2.36, 0.24; 2.66, 0.08; 2.96, 0.03; 3.26, 0.04; 3.56, 0.05; 3.86, 0.06; 4.16, –0.11; 4.46, 0.01; 4.76, 0.02.

$[\mathrm{H}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Hg}]_\mathrm{o} = 0.00984$ M, $[\mathrm{Td}]_\mathrm{o} = 0$ M, $[\mathrm{H}]_\mathrm{T} = 0.0100$ M, $[\mathrm{Hg}]_\mathrm{T} = 0$ M, $[\mathrm{Td}]_\mathrm{T} = 1.016$ M.
Vo = 95.00 cm^3.
0.20, 6.77; 0.45, 8.30; 0.70, 8.27; 0.95, 8.46; 1.20, 8.60; 1.46, 8.96; 1.71, 8.60; 1.96, 4.91; 2.21, 0.67; 2.46, 0.23; 2.71, 0.12; 3.21, 0.18; 3.46, 0.07; 3.71, 0.13; 3.96, 0.13; 4.22, 0.08; 4.47, 0.13; 4.72, 0.14; 4.97, 0.08.

$[\mathrm{H}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Hg}]_\mathrm{o} = 0.00984$ M, $[\mathrm{Td}]_\mathrm{o} = 0$ M, $[\mathrm{H}]_\mathrm{T} = 0.0100$ M, $[\mathrm{Hg}]_\mathrm{T} = 0$ M, $[\mathrm{Td}]_\mathrm{T} = 1.016$ M.
Vo = 95.00 cm^3.
0.26, 8.92; 0.59, 10.80; 0.92, 11.25; 1.24, 11.20; 1.57, 11.44; 1.90, 8.90; 2.23, 1.14; 2.55, 0.26; 2.88, 0.16; 3.21, 0.21; 3.54, 0.11; 3.86, 0.16; 4.19, 0.17; 4.52, 0.11; 4.85, 0.12; 5.18, 0.12; 5.50, 0.12.

(iii) System: Ag^+ + thiourea.
$[\mathrm{Ag}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Tu}]_\mathrm{o} = 0$ M, $[\mathrm{Ag}]_\mathrm{T} = 0$ M, $[\mathrm{Tu}]_\mathrm{T} = 1.004$ M. Vo = 95.00 cm^3.
0.26, 20.26; 0.56, 23.68; 0.86, 23.14; 1.16, 20.13; 1.47, 14.40; 1.77, 3.66; 2.07, 3.13; 2.37, 2.26; 2.67, 1.60; 2.97, 0.93; 3.27, 0.71; 3.58, 0.31; 3.88, 0.65; 4.18, 0.24; 4.48, 0.24; 4.78, 0.35.

$[\mathrm{Ag}]_\mathrm{o} = 0.0100$ M, $[\mathrm{Tu}]_\mathrm{o} = 0$ M, $[\mathrm{Ag}]_\mathrm{T} = 0$ M, $[\mathrm{Tu}]_\mathrm{T} = 1.004$ M. Vo = 95.00 cm^3.
0.19, 14.86; 0.44, 19.34; 0.69, 19.06; 0.93, 18.95; 1.18, 15.43; 1.43, 12.26; 1.67, 3.01; 1.92, 2.92; 1.17, 2.33; 2.41, 1.62; 2.66, 1.07; 2.91, 0.74; 3.15, 0.68; 3.40, 0.45; 3.65, 0.39; 3.89, 0.34.

(iv) System: Hg^{2+} + thiourea
$[\mathrm{H}]_\mathrm{o} = 0.4668$ M, $[\mathrm{Hg}]_\mathrm{o} = 9.93 \times 10^{-3}$ M, $[\mathrm{Tu}]_\mathrm{o} = 0$ M, $[\mathrm{H}]_\mathrm{T} = 0.4966$ M, $[\mathrm{Hg}]_\mathrm{T} = 0$ M, $[\mathrm{Tu}]_\mathrm{T} = 1.000$ M.
Vo = 95.00 cm^3.
0.24, 17.47; 0.54, 21.49; 0.83, 21.04; 1.13, 21.41; 1.42, 20.84; 1.72, 20.42; 2.01, 20.82; 2.31, 10.59; 2.60, 6.73; 2.90, 5.96; 3.19, 4.97; 3.49, 3.95; 3.78, 3.20; 4.08, 2.39; 4.37, 1.95.

$[\mathrm{H}]_\mathrm{o} = 0.4668$ M, $[\mathrm{Hg}]_\mathrm{o} = 9.93 \times 10^{-3}$ M, $[\mathrm{Tu}]_\mathrm{o} = 0$ M, $[\mathrm{H}]_\mathrm{T} = 0.4966$ M, $[\mathrm{Hg}]_\mathrm{T} = 0$ M, $[\mathrm{Tu}]_\mathrm{T} = 1.000$ M.
Vo = 95.00 cm^3.
0.24, 17.68; 0.57, 23.38; 0.89, 23.14; 1.22, 23.06; 1.54, 23.25; 1.86, 24.46; 2.19, 18.45; 2.51, 7.60; 2.84, 6.90; 3.16, 5.63; 3.48, 4.46; 3.81, 3.43; 4.13, 2.68; 4.46, 1.96; 4.78, 1.64; 5.10, 1.30.

(v) System: Cd^{2+} + thiourea.
$[\mathrm{H}]_\mathrm{o} = 0$ M, $[\mathrm{Cd}]_\mathrm{o} = 0.009725$ M, $[\mathrm{Tu}]_\mathrm{o} = 0$ M, $[\mathrm{H}]_\mathrm{T} = 0$ M, $[\mathrm{Cd}]_\mathrm{T} = 0$ M, $[\mathrm{Tu}]_\mathrm{T} = 1.012$ M. Vo = 95.00 cm^3.
0.28, 0.89; 0.60, 1.04; 0.92, 0.95; 1.24, 0.97; 1.56, 0.88; 1.87, 0.84; 2.19, 0.74; 2.51, 0.70; 2.83, 0.76; 3.15, 0.72; 3.47, 0.62; 3.79, 0.63; 4.11, 0.64; 4.43, 0.59.

$[\mathrm{H}]_\mathrm{o} = 0$ M, $[\mathrm{Cd}]_\mathrm{o} = 0.01945$ M, $[\mathrm{Tu}]_\mathrm{o} = 0$ M, $[\mathrm{H}]_\mathrm{T} = 0$ M, $[\mathrm{Cd}]_\mathrm{T} = 0$ M, $[\mathrm{Tu}]_\mathrm{T} = 1.012$ M. Vo = 95.00 cm^3.
0.37, 1.97; 0.78, 2.17; 1.18, 2.09; 1.59, 1.89; 2.00, 1.86; 2.41, 1.71; 2.82, 1.61; 3.22, 1.63; 3.63, 1.48; 4.04, 1.49; 4.45, 1.39.

(vi) System: Hg^{2+} + sulphite
$[\mathrm{H}]_\mathrm{o} = 0$ M, $[\mathrm{Hg}]_\mathrm{o} = 0$ M, $[\mathrm{SO_3}]_\mathrm{o} = 0.002904$ M, $[\mathrm{H}]_\mathrm{T} = 0$ M, $[\mathrm{Hg}]_\mathrm{T} = 0.03936$ M, $[\mathrm{SO_3}]_\mathrm{T} = 0$ M. Vo = 95.00 cm^3.
0.18, 0.63; 0.45, 0.95; 0.71, 0.74; 0.98, 0.97; 1.24, 0.98; 1.50, 0.99; 1.77, 0.89; 2.03, 0.95; 2.30, 0.79; 2.56, 1.02.

TABLE III (*continued*)

$[H]_o = 0$ M, $[Hg]_o = 0$ M, $[SO_3] = 0.002904$ M, $[H]_T = 0$ M, $[Hg]_T = 0.03936$ M, $[SO_3]_T = 0$ M. Vo = 95.00 cm^3.
0.13, 0.70; 0.37, 0.93; 0.62, 0.94; 0.86, 0.90; 1.10, 1.02; 1.34, 1.08; 1.59, 0.76; 1.83, 0.94; 2.07, 1.00; 2.31, 0.95; 2.56, 0.85.

$[H]_o = 0$ M, $[Hg]_o = 0$ M, $[SO_3]_o = 0.002904$ M, $[H]_T = 0$ M, $[H]_T = 0.03936$ M, $[SO_3]_T = 0$ M,
Vo = 95.00 cm^3.
0.17, 0.86; 0.44, 0.76; 0.71, 0.98; 0.97, 0.83; 1.24, 1.05; 1.50, 0.90; 1.77, 0.96; 2.03, 1.13; 2.30, 0.92; 2.56, 1.04; 2.83, 0.77.

Silver(I) Thiodiglycol

This system presented no particular difficulty, and the results obtained for the stability constants and the thermodynamic quantities of complex formation are given in Table IV.

Mercury(II) Thiodiglycol

The stability constants and the thermodynamic quantities of complex formation are given in Table IV.

Silver(I) Thiourea

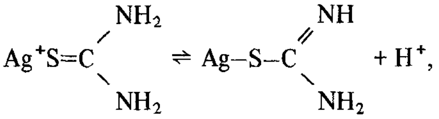
The complexes formed by this system decompose readily to precipitate AgS. Decomposition occurs only when the ligand solution is added slowly to the Ag^+ solution, which indicates that it is a lower complex, probably the AgL complex, that is unstable. It was found that decomposition could be avoided by the presence of 0.01 M $HClO_4$ and by elimination of most of the supporting electrolyte by adjustment of the ionic strength to 0.02 M with $NaClO_4$. The influence of H^+ may be the prevention

TABLE IV

Stability constants, β_i, together with the free energy ΔG_i°, enthalpy ΔH_i°, and entropy changes (expressed as the entropy contribution to the free energy of complex formation, $T\Delta S_i^\circ$) of complexation of the metal M with ligand L at 298.15 K and the ionic strength indicated.

Metal	Ligand	Ionic strength μ/M	Complexes	log β_i (molarity units)	ΔG_i°/ kJ.mol^{-1}	ΔH_i°/ kJ.mol^{-1}	$T\Delta S_i^\circ$/ kJ.mol^{-1}
Ag	thiodiglycol	0.5	AgL^+	3.53 ± 0.06	−20.1 ± 0.3	−31.6 ± 0.6	−11.5 ± 0.7
			AgL_2^+	5.81 ± 0.05	−33.2 ± 0.3	−66.5 ± 1.1	−33.3 ± 1.1
			AgL_3^+	6.68 ± 0.15	−38.1 ± 0.9	−75 ± 7	−37 ± 7
Hg	thiodiglycol	0.5	HgL^{2+}	6.37 ± 0.17	−36.4 ± 1.0	−33.3 ± 0.8	3.1 ± 1.3
			HgL_2^{2+}	10.47 ± 0.06	−59.8 ± 0.3	−69.6 ± 1.1	−9.8 ± 1.1
			HgL_3^{2+}	11.5 ± 0.2	−65.6 ± 1.1	−62 ± 19	4 ± 19
			HgL_4^{2+}	14.1 ± 0.7	−80.5 ± 4.0	−70 ± 3	10 ± 5
Ag	thiourea	0.02	AgL^+	6.46 ± 0.10	−39.6 ± 0.6	−81 ± 3	−44 ± 3
			AgL_2^+	10.90 ± 0.07	−62.2 ± 0.4	−113 ± 5	−51 ± 5
			AgL_3^+	12.88 ± 0.09	−73.5 ± 0.5	−127 ± 7	−54 ± 7
			$Ag_2L_3^{2+}$	20.73 ± 0.18	−118.3 ± 1.0	−217 ± 7	−99 ± 7
Hg	thiourea	0.5	HgL^{2+}	11.4 ± 0.9	−65 ± 5	−74 ± 11	−9 ± 11
			HgL_2^{2+}	22.11 ± 0.05	−126.2 ± 0.3	−144 ± 9	−18 ± 9
			HgL_3^{2+}	25.15 ± 0.03	−143.6 ± 0.2	−188 ± 13	−44 ± 13
			HgL_4^{2+}	27.10 ± 0.05	−154.7 ± 0.3	−203 ± 20	−48 ± 20
			$Hg_2L_3^{4+}$	36.0 ± 0.4	−205 ± 2	−210 ± 24	−5 ± 24
Cd	thiourea	0.5	CdL^{2+}	1.32(26)	−7.53	−19.3 ± 0.8	−11.8 ± 0.8
			CdL_2^{2+}	2.04(26)	−11.6	−41 ± 4	−29 ± 4
			CdL_3^{2+}	2.20(26)	−12.6	–	–
			CdL_4^{2+}	3.04(26)	−17.4	–	–
Hg	sulphite	0.5	HgL_2^{2-}	23.33 ± 0.02	−133.2 ± 0.1	91 ± 7	42 ± 7
			HgL_3^{4-}	24.1 ± 0.3	−138 ± 2	–	–

of deprotonation of the Ag-thiourea complex



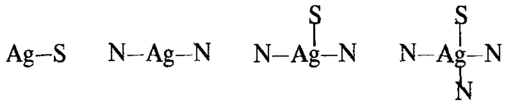
$$Ag^+S{=}C(NH_2)_2 \rightleftharpoons Ag{-}S{-}C({=}NH)NH_2 + H^+,$$

which could be the first step towards decomposition of the complex to form AgS. The role of the supporting electrolyte is not clear, but may be the stabilization of a charged transition state.

Potentiometric data for this system were obtained at an overall metal concentration of 4×10^{-3} M, and the calorimetric data were obtained at $[Ag]_T = 10^{-2}$ M. It was found that the data could not be adequately described by stability-constant data available in the literature,[20,21] which had been obtained potentiometrically at a lower overall metal concentration ($10^{-4} - 10^{-6}$ M). It was found that the introduction of a polynuclear Ag_2L_3 complex into the calculations produced a vastly improved fit to the data, particularly at a mole ratio of L to Ag of approximately 1.5. Recently, charge-transfer spectra[22] have given evidence for the existence of similar polynuclear complexes for Cu(I) thiourea.

The stability constants and the thermodynamic quantities of complex formation are given in Table IV. The enthalpy changes may be compared with those of Berthon and Luca,[20] i.e., $\Delta H_1^\circ = -10.9$, $\Delta H_2^\circ = -91.8$, and $\Delta H_3^\circ = -96.5$ kJ mol^{-1}.

Enea and Berthon[23] regarded the small values found by Berthon and Luca for the first and third, compared with the large second and fourth stepwise enthalpy changes, as evidence that both the S and N atoms of thiourea are involved in bond formation in the mononuclear complexes as follows:



(i) (ii) (iii) (iv)

When the polynuclear $Ag_2L_3^{2+}$ complex is taken into account, a more usual sequence of ΔH_1°, ΔH_2°, and ΔH_3° is obtained (see Table IV). This sequence seems to indicate that the same donor atom, probably the S atom, is involved in all the mononuclear complexes. Because of the improvement of fit obtained with the introduction of a polynuclear complex, and because of the simpler view of the bonding position, it is felt that the results of Table IV are to be preferred to those of Berthon and Luca.

Mercury(II) Thiourea

Like the silver(I) thiourea complexes, these complexes are stable only in the presence of excess acid. Therefore, in this instance, the ionic strength was made up to 0.5 M with perchloric acid, for both potentiometric and calorimetric titrations. Potentiometric titrations were done at $[Hg]_T = 0.01$ M, and, as for silver(I) thiourea, there was some evidence for the formation of the polynuclear Hg_2L_3 complex, indicated by an improved χ^2 'goodness of fit' statistic from the MINIQUAD programme.

The stability constants and the thermodynamic quantities of complex formation are given in Table IV.

Cadmium(II) Thiourea

Stability constants reported by Migal' and Tsiplyakova,[24] i.e., $\log \beta_1 = 1.32$ and $\log \beta_2 = 2.04$ obtained at 298.15 K and $\mu = 0.01$ M, were used for derivation of values of ΔH_i° from titration-calorimetric data. There was no evidence of the existence of higher complexes at the concentrations used in the experiment.

It can be shown readily that the variation of stability constants of mononuclear complexes with ionic strength is given, in general, by

$$\log \beta_i^{\mu} = \log \beta_i^{\mu=0} + (\log \gamma_M^{\mu}\, n^+ + i \log \gamma_L^{\mu}\, m^- - \log \gamma^{\mu}_{ML_i(n-im)^+}) \qquad (2)$$

According to the Davies extension[25] of the Debye–Hückel limiting activity equation, the activity coefficient of an ionic species at a given ionic strength depends (to a good approximation for fairly dilute solutions) only on its charge. Therefore, it follows that, for neutral ligands, $\log \beta$ should be independent of ionic strength to a first approximation. The results obtained for this system are given in Table IV.

Mercury(II) Sulphite

The species $HgSO_3$ was found to be unstable, so the usual order of titration was reversed, and the mercuric perchlorate solution was added to the Na_2SO_3 solution, care being taken not to reach a ratio of metal to ligand of 1.

The stability constants obtained by potentiometric titration, together with the thermodynamic quantities of complex formation, are given in Table IV. The stability constants can be compared with a value of $\log \beta_2 = 22.85$ obtained by Toropova and Belaya[27] at 291.15 K and $\mu = 3$ M, and $\log \beta_2 = 24.07$ and $\log \beta_3 = 24.96$ at 291.15 K and $\mu \to 0$.

DISCUSSION AND CONCLUSIONS

For the calculation of the stability constants from potentiometric data, both the LETAGROP VRID and the MINIQUAD programmes were used. The advantages of MINIQUAD over other programmes for calculation of formation constants have been discussed.[10] It was confirmed in this investigation that MINIQUAD is some twenty to thirty times faster than LETAGROP. However, a difficulty encountered in the use of MINIQUAD for testing of alternative models is that, when a negative value of β_i is encountered at the end of an iteration cycle, that formation constant is set equal to zero, and eliminated from subsequent calculations. It is found that if different models are proposed initially with the same set of data, different constants may be eliminated, so that a complex that is eliminated in calculations with one model may be retained and given a value of β_i with another model. Obviously, for complicated systems, an attempt should be made to gain further experimental evidence for the existence of the more exotic of the postulated species.

Examination of Table IV shows that, for the complexes studied, the greater stability of Hg(II) complexes are compared with the analogous Ag(I) complexes is mainly an entropy effect. The free energies of formation of the Hg(II) thiourea and thiodiglycol complexes are approximately twice those of the analogous Ag(I) complexes, whereas the enthalpy changes on complex formation are similar. For sulphite, the free-energy change on complex formation is nearly three times as large as for Ag(I), whereas the enthalpy change is only twice as large.

Cobble[29-31] extended the semi-empirical equations developed by Powell and Latimer[32] for the calculation of standard partial molar entropies of non-electrolytes in aqueous solution to the calculation of $\bar{S}^\circ$ of inorganic complexes formed with neutral ligands. The main assumption made in doing so was that the charge on the complex was sufficiently shielded from the solvent for it to be regarded as a non-electrolyte. The expression obtained was

$$\bar{S}^\circ = 10 + 3/2R \ln M + 9.2N - \bar{S}_s^\circ - 0.22V_m \tag{3}$$

with a slight modification above $N = 14$, where M is the molecular mass of the complex, N is the number of skeletal atoms (i.e., not including hydrogen atoms), $\bar{S}_s^\circ$ are empirically derived entropy contributions of structural features such as double bonds, rings, etc., and V_m is the molar volume.

For the generalized complex-formation reaction involving neutral ligands for which it can be assumed that the charge on the resulting complex is shielded from the solvent

$$M(\mathrm{H_2O})_x + nL = ML_n + x\mathrm{H_2O} \tag{4}$$

$\bar{S}^\circ$ for all the species taking part in the reaction is known, or can be calculated from equation (3). If ΔS° for the overall reaction is measured, then the value of x can be calculated. This approach was used by Curthoys[33] to calculate that x equals zero for the $\mathrm{Ag^+}$ aquo ion.

It can be shown from equation 3 that, for two metal ions of similar size, M and M', the entropy of the complexes formed with the same ligand L, i.e., ML_n and $M'L_n$, are nearly equal. If we then assume that, for the two metal ions, x is the same for the same values of n, it can be seen that the only major difference in ΔS° for their analogous complex-formation reactions should be the difference in $\bar{S}^\circ$ of their respective metal aquo ions. The entropy of $\mathrm{Hg^{2+}(aq)}$ and $\mathrm{Ag^{+}(aq)}$ are -22.6 and $+73.93$ J K^{-1} mol^{-1} respectively,[34] which suggests a constant difference of 28.8 kJ mol^{-1} in $T\Delta S^\circ$ on complex formation. The mean difference between $T\Delta S^\circ$ on formation of analogous Ag(I) and Hg(II) complexes in Table IV is 25 kJ mol^{-1}. Therefore, in the absence of any great difference in the enthalpy changes on complex formation, the greater stability of the Hg(II) complexes is purely a function of the more negative $\bar{S}^\circ$ of the $\mathrm{Hg^{2+}}$ as compared with the $\mathrm{Ag^+}$ aquo ion.

Although Curthoys[33] suggested that the value of x equal to zero in equation (4) indicates that there is no firmly bound water on the $\mathrm{Ag^+}$ aquo ion, this conclusion must be approached with some caution. For example, Cobble tested his equation on the Ni(ethylenediamine)$_3^{2+}$ complex and, using ΔS_3° reported[35] as 172 J K^{-1} mol^{-1}, found his results to be consistent with $x = 6$, which would be expected for Ni(II). More recent values[2] centre on -37 J K^{-1} mol^{-1}, which is consistent with $x \approx 3$, not normally acceptable as a reasonable value for the coordination number of the Ni(II) ion.

Therefore, it would seem that the values of x obtained in this way should not be interpreted too literally.

TABLE V

Experimental values of ΔS°_2 and ΔS°_3 for Ag^+, Hg^{2+} and Cd^{2+} with the ligands thiodiglycol and thiourea, together with $\bar{S}^{\circ exp}_{ML_n}$ and calculated values of $\bar{S}^{\circ}_{ML_n}$ at $x = 0$, and $\bar{S}^{\circ}_{ML_n}$ for the value of x producing the closest agreement with $\bar{S}^{\circ exp}_{ML_n}$.

Metal ion	Ligand	Complex	ΔS°_n/ J.K.$^{-1}$ mol^{-1}	$\bar{S}^{\circ exp}_{ML_n}$ J.K.$^{-1}$ mol^{-1}	$\bar{S}^{\circ}_{ML_n}(x=0)$ J.K.$^{-1}$ mol^{-1}	$\bar{S}^{\circ}_{ML_n}(x)$ J.K.$^{-1}$ mol^{-1}	x
Ag^+	Thiodiglycol	AgL_2^+	−111 ± 4	515 ± 17	497	497	0
		AgL_3^+	−124 ± 23	778 ± 31	575	795	3
Hg^{2+}	Thiodiglycol	HgL_2^{2+}	−33 ± 4	496 ± 17	528	528	0
		HgL_3^{2+}	13 ± 64	818 ± 67	613	833	3
		HgL_4^{2+}	34 ± 17	1115 ± 29	651	1090	6
Ag^+	Thiourea	AgL_2^+	−171 ± 17	185 ± 24	286	213	−1
		AgL_3^+	−181 ± 23	317 ± 31	330	330	0
Hg^{2+}	Thiourea	HgL_2^{2+}	−60 ± 30	200 ± 34	307	234	−1
		HgL_3^{2+}	−148 ± 44	253 ± 49	357	284	−1
		HgL_4^{2+}	−161 ± 67	381 ± 71	403	403	0
Cd^{2+}	Thiourea	CdL_2^{2+}	−97 ± 13	124 ± 21	288	142	−2

The application of equation (3) to these results is interesting, if the uncertainty in the interpretation of x is borne in mind. For the Hg(II) and Ag(I) thiodiglycol complexes, it is found that, for $n = 1$ and 2, x = zero, as was found by Curthoys for Ag(I) amine complexes. However, for n equals three, x equals three for both Hg(II) and Ag(I), as seen in Table V, and x equals six for n equals four for Hg(II). Therefore, it may be that no water is displaced for complexes having n equals two, rather than that there is no water strongly coordinated to Hg(II) or Ag(I). It appears that the water molecules are displaced when further ligands are coordinated. It is tempting, on this basis, to speculate that, in fact, the favoured coordination number of two encountered in these metal ions results because the first two ligands can be coordinated without displacement of water, but that coordination of further ligands requires that water should be displaced, and results in small values of log K_3 and log K_4. For the thiourea complexes, this pattern is not observed. However, in view of the existence of a canonical form of the thiourea molecule involving a positive charge on the nitrogen atoms,[36] it is possible that, to a large extent, the charge on the thiourea complexes is located on the nitrogen, i.e., on the surface of thiourea complexes coordinated through the sulphur. This suggests that the values of x observed in fact reflect a breakdown in the assumption that the charge is shielded from the solvent, rather than any real addition of water, as might be inferred from Table V.

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