Metal Complexes Involving the Heavier Donor Atoms. Part V.[1] Stability and Heats of Formation of Silver(I), Cadmium(II), and Lead(II) Complexes of Semicarbazide, Thiosemicarbazide, and Selenosemicarbazide

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Stability constants of complexes of silver(I) with semicarbazide (sc), thiosemicarbazide (tsc), and selenosemicarbazide (ssc) have been measured by a metal-electrode method and those of cadmium(II) and lead(II) by a polarographic method. The heats of formation of these complexes have been measured calorimetrically. The free energy and enthalpy of formation of the silver(I) complexes follow the normal class ' b ' donor-atom sequence $O \ll S < Se$. For cadmium(II) and lead(II), although the general affinity order is similar, there are exceptions.

PREVIOUS thermodynamic studies [1,2] of metal complexes of semicarbazide and its sulphur and selenium analogues have now been extended to include silver(I), a typical class ' b ' [3] metal ion, and cadmium(II) and lead(II), both borderline class ' a '–class ' b ' metal ions. Other workers have isolated solid complexes [4–6] of silver(I) with thiosemicarbazide in which the metal : ligand ratio is 1 : 1, 1 : 2, 2 : 3, and 1 : 3, and have determined the stability constant of the 1 : 3 complex.[7] Solid complexes of cadmium(II) with semicarbazide [8] and thiosemicarbazide [9] are known and the stability, but not the heats of formation, of complexes with all three ligands have been measured.[2,10] There appears to be no previous work on lead(II) complexes with any of these ligands.

EXPERIMENTAL

The ligands were prepared as described previously.[2] Because solutions of selenosemicarbazide decomposed readily to give a red precipitate of selenium, these were prepared as when needed and their containers were wrapped in dark paper. Such solutions could be kept for 1 h without appreciable decomposition. Stock silver(I) solutions were standardised using pure sodium chloride, and lead(II) and cadmium(II) solutions using EDTA.

RESULTS

Preliminary Potentiometric Titrations of Silver(I).—Pure silver wire was used as the indicator electrode.

With thiosemicarbazide. When 10mM-AgNO$_3$ (in 10mM-HNO$_3$) was titrated with 10mM-thiosemicarbazide (in 10mM-HNO$_3$), a white precipitate appeared when the ratio Ag : tsc

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[1] Part IV, S. O. Ajayi and D. R. Goddard, *J. Chem. Soc.* (*A*), 1971, 2673.

[2] D. R. Goddard, B. D. Lodam, S. O. Ajayi, and M. J. Campbell, *J. Chem. Soc.* (*A*), 1969, 506.

[3] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 256.

[4] V. Harley, *Chem. Abs.*, 1936, **30**, 8059.

[5] G. F. Gasparri, A. Mangia, A. Musatti, and M. Nardelli, *Acta Cryst.*, 1968, **B24**, 367; M. Nardelli, G. G. Fava, and I. Chierici, *Chem. Abs.*, 1966, **64**, 11973.

[6] W. I. Stephen and A. Townshend, *J. Chem. Soc.* (*A*), 1966, 166.

[7] V. F. Toropova and L. S. Kirillova, *Russ. J. Inorg. Chem.*, 1960, **5**, 276.

[8] G. S. Smith, *J. Chem. Soc.*, 1937, 1356.

[9] M. Nardelli and I. Chierici, *Ricerca sci.*, 1960, **30**, 276.

[10] V. F. Toropova and K. V. Naumushina, *Russ. J. Inorg. Chem.*, 1960, **5**, 421; A. N. Christensen and S. E. Rasmussen, *Acta Chem. Scand.*, 1963, **17**(5), 1315.

(tsc = thiosemicarbizide) was 1 : 0·5, increased in quantity, and finally redissolved when the ratio became 1 : 2·2. An inflexion in the potential curve occurred when the ratio was 1 : 1. Analysis of the precipitate (Table 1) showed a composition [Ag(tsc)]NO$_3$ when the ratio was between 1 : 0·75 and 1 : 1, and [Ag$_2$(tsc)$_3$](NO$_3$)$_2$ when the ratio was between 1 : 1·5 and 1 : 2. Silver(I) and sulphur were determined gravimetrically and nitrogen microanalytically by the Dumas method.

TABLE 1

Analysis (%) of precipitated silver(I) thiosemicarbazide complexes

Molar ratio Ag : tsc	Ag	S	N
1 : 0·75	41·4	13·1	22·5
1 : 1	41·0	12·5	21·9
1 : 1·5	35·3	15·4	25·5
1 : 2	35·0	15·1	25·6
Calc. for [Ag(tsc)](NO$_3$):	41·3	12·3	21·5
Calc. for [Ag$_2$(tsc)$_3$](NO$_3$)$_3$:	35·2	15·7	25·1

With selenosemicarbazide. When 10mM-AgNO$_3$ (in 20mM-HNO$_3$) was titrated with 10mM-selenosemicarbazide (in 20mM-HNO$_3$), a black precipitate formed immediately. An inflexion in the potential curve occurred when the ratio Ag : ssc (ssc = selenosemicarbazide) was 1 : 0·5 which indicated that the precipitate was Ag$_2$Se due to decomposition. The reverse titration gave an inflexion at the ratio Ag : ssc of 1 : 1·5 and precipitation did not occur until the ratio was reduced to 1 : 1·2.

With semicarbazide. Similar titrations to the above showed no precipitation or inflexion in the potential curve.

Stability of the Silver(I) *Complexes.*—The electrical-potential method using the cell (1) was employed. Electrodes were prepared by silver-plating platinum[11] and

$$\mathrm{Hg|Hg_2Cl_2,KCl(sat.)|2M\text{-}NH_4NO_3|}\ \text{Solution of silver(I) and ligand}|\mathrm{Ag} \quad (1)$$

checked for reproducibility (to within 0·3 mV) using pure silver(I) solutions. A fresh electrode was used for each titration. All measurements were made at 30 °C.

With semicarbazide. Silver(I) nitrate (5—25mM) was titrated with semicarbazide (200mM). All solutions were in 10mM-HNO$_3$ and the ionic strength was made 0·1M by addition of KNO$_3$. The results were treated by the Leden–Fronaeus method as described by Chatt[12] and values of β_1 and β_2 obtained.

With thiosemicarbazide. Several different methods were used.

(*a*) *Leden–Fronaeus titration.* Silver(I) nitrate (1—20mM) was titrated with thiosemicarbazide (40—100mM) using ligand : metal ratios greater than 2 : 1 (to avoid precipitation). All solutions were in 10 or 20mM-HNO$_3$ and the ionic strength was 0·03M. Values for β_2 and β_3 only were obtained from the results.

(*b*) *Leden–Fronaeus titration* [*silver*(I) *concentration constant*]. Silver(I) concentrations were kept constant by the addition of silver(I) together with the ligand, thereby avoiding the crossing of E_M against c_L titration curves which were obtained when silver(I) concentrations became very low [c_L = total ligand concentration; E_M = e.m.f. (ligand absent) − e.m.f. (ligand present)].

(*c*) *Hedstrom's method.* The results of the previous titration were recalculated by the Hedstrom method.[13] The parameter $F_1 = (c_M - [M])/[M][L]$ was constant for each value of the free-ligand concentration [L] and independent of the free-metal concentration [M], showing that no polynuclear species were present (c_M = total metal concentration).

(*d*) *Successive approximation method.* Individual mixed solutions were used in place of the titration method. This enabled higher concentrations of the less-soluble selenosemicarbazide to be obtained. The calculation was similar to that in (*a*); [L] was initially assumed to be equal to c_L. Approximate values of β_2 and β_3 were obtained which were then used to obtain better values of [L] and the process repeated until β values and [L] were constant. The results of the different methods are given in Table 2.

With selenosemicarbazide. Because solutions of this ligand decomposed readily and because of the low solubility of this ligand (*ca.* 0·04M), the successive-approximation method only was used. Silver(I) concentrations were 1 and 2mM, HNO$_3$ 5mM, selenosemicarbazide 4—30mM, and I = 0·01M.

TABLE 2

Stability constants of silver(I) thiosemicarbazide complexes at 30 °C with standard deviations in parentheses

Method	β_2/ l^2 mol^{-2}	β_3/ l^3 mol^{-3}
(*a*) Leden–Fronaeus:		
Titration with 40mM-tsc	4·3(0·7) × 10^{10}	
Titration with 100mM-tsc	4·6(0·5) × 10^{10}	4·9(0·3) × 10^{12}
(*b*) Leden–Fronaeus:		
Total silver concn. constant	3·0(0·1) × 10^{10}	3·7(0·1) × 10^{12}
(*c*) Hedstrom's method applied to the experimental data of (*b*)	4·1(0·5) × 10^{10}	3·0(0·4) × 10^{12}
(*d*) Successive approximation		
1mM-Ag^{I}	2·5(0·3) × 10^{10}	2·0(0·1) × 10^{12}
2mM-Ag^{I}	3·0(0·3) × 10^{10}	1·9(0·1) × 10^{12}
Mean values	3·6(0·4) × 10^{10}	3·1(0·6) × 10^{12}

Cadmium(II) *and Lead*(II) *Complexes.*—*Stability measurements.* A polarographic method similar to that of Lane *et al.*[14] was used. Polarograms were recorded manually using a potentiometer with a precision of 0·1 mV for the voltage reading and the current reading (by measuring the voltage across a 10 000 Ω resistance). The resistance of the cell was measured independently using a.c. in order to correct for the *IR* drop across the cell. Solutions contained 1mM-metal ion and varying concentrations of ligand [10—450mM-sc (sc = semicarbazide), 1—80mM-tsc, or 1—40mM-ssc], 10mM-HNO$_3$, gelatin (0·01%), and their ionic strength was adjusted to 0·1M with potassium nitrate. The experimental data were treated by the method of Deford and Hume.[15] Initially, values of the stability constants were obtained by assuming that the free-ligand concentration [L] was equal to c_L, and then these values were improved by successive approximation.

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[11] S. Brown, *J. Amer. Chem. Soc.*, 1934, **54**, 646.

[12] S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 1958, 274.

[13] B. Hedstrom, *Acta Chem. Scand.*, 1955, **9**, 613.

[14] T. J. Lane, J. A. Ryan, and E. F. Britten, *J. Amer. Chem. Soc.*, 1958, **80**, 315.

[15] D. D. Deford and D. H. Hume, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.

Lead(II) ions, unlike those of cadmium(II) and silver(I), associate considerably with nitrate ions and several workers [16–18] have measured the stability constant of $[PbNO_3^+]$. In consequence, stability constants calculated initially from our polarographic measurements were in effect conditional constants. By assuming that the activity coefficients $f(PbX_n^{2+}) = f(Pb^{2+})$ (X = neutral ligand) and $f(PbNO_3^+) \doteqdot f(NO_3^-)$, it is easily shown that the stability constants obtained by De Ford and Hume's method, neglecting the nitrate-ion association, are related to the true constants by equation (2), where K is the stability constant of $[PbNO_3]^+$.

$$\beta_{\text{true}} = \beta_{\text{apparent}} \cdot \{1 + K[NO_3^-]f(Pb^{2+})\} \quad (2)$$

We chose to use the value $K = 12$ l mol^{-1} obtained by Nyman *et al.*[17] at 25 °C using a polarographic method. Since, according to Nancollas,[18] the value of the enthalpy of formation of $[PbNO_3]^+$ is only −0·57 kcal mol^{-1}, the value of K at 30 °C will be little different from that at 25 °C. The activity coefficient $f(Pb^{2+})$ was calculated to be 0·38 at I = 0·1M, using the Guggenheim equation, and a 'b' value of 0·7, following Nyman *et al.*[17] Thus in the 0·1M-nitrate-ion solutions used, the true stability constants were obtained by multiplying the apparent constants by 1·46.

Calorimetric measurements. The calorimeter and general method of measurement were similar to those already described.[2] Metal nitrate solution (20 cm^3) was placed in the doubly stoppered bottle and ligand solution (850 cm^3) in the Dewar vessel. Final total concentrations were similar to those used in the stability measurements, and the concentration of the individual species present in the mixed solution were calculated from the stability constants. Correction was made for the heat of dilution of the metal-ion solution [normally very small, but very large and endothermic in the case of lead(II)] by separate dilution experiments, and also for the change in protonation of the ligand by use of known ionisation constants and heats of protonation.[2] Normally two complex species were present and, by varying the composition over a wide range, the heats of formation of each species could be obtained by solving the simultaneous equations graphically. Enthalpy values for the lead(II) complexes were initially calculated by neglecting the association of lead(II) and nitrate ions. The true enthalpy values were obtained by correcting for the heat absorbed in dissociating the $[PbNO_3]^+$ complexes present as in equation (3). Using $\Delta H(PbNO_3^+)$

$$\Delta H_{\text{true}} = \Delta H_{\text{apparent}} + [\Delta H(PbNO_3^+)K[NO_3^-]f(Pb^{2+})]/\{1 + K[NO_3^-]f(Pb^{2+})\} \quad (3)$$

= −0·57 kcal mol^{-1}, the correction term is only −0·2 kcal mol^{-1}. Further details of the calculations of the heats of formation of the silver(I), cadmium(II), and lead(II) complexes are to be found in Supplementary Publication No. SUP 20710 (6 pp., 1 microfiche).*

DISCUSSION

The formation of two insoluble silver complexes [Ag(tsc)](NO$_3$) and [Ag(tsc)$_3$](NO$_3$)$_2$ is in accord with earlier work.[4,6] It is probable that both complexes are polymeric as in the case of [Ag(tsc)]Cl.[5] The corresponding complexes with selenosemicarbazide, if formed, are unstable with respect to silver(I) selenide.

The results of stability-constant determinations are summarised in Table 3. The only previously reported stability constant for silver(I) complexes with these ligands, that of [Ag(tsc)$_3^+$] (log$_{10}$ β_3 12·54 at 30 °C),[7] agrees well with our result. Our values for the stability constants of the cadmium(II) complexes we consider to be more reliable than those obtained by a preliminary polarographic determination which we reported earlier,[2] and it is significant that the values are in better agreement with those, also obtained previously, using a cadmium amalgam electrode. Constants were obtained for lead(II) complexes with one and two molecules of ligand in the case of semicarbazide, but only with one molecule in the case of the sulphur and selenium analogues because of the much lower solubility of these two ligands.

TABLE 3

Summary of stability constants at 30 °C and I = 0·1M, except where stated otherwise. Standard deviations are in parentheses

		Semicarbazide	Thiosemicarbazide	Selenosemicarbazide
Ag^{I}	β_1*	9·0(0·1) × 10^1		
	β_2	5·0(0·9) × 10^2	3·6(0·4) × 10^{10} [a]	4·8(0·8) × 10^{13} [b]
	β_3		3·1(0·6) × 10^{12} [a]	4·2(0·4) × 10^{15} [b]
Cd^{II}	β_1	1·8(0·4) × 10^1	1·9(0·1) × 10^2	8·3(0·6) × 10^2
	β_2	6·2(0·4) × 10^2	2·5(0·4) × 10^4	1·1(0·1) × 10^5
Pb^{II} [c]	β_1	1·3(0·1) × 10^2	7·7(0·3) × 10^2	1·9(0·3) × 10^2
	β_2	7·2(1) × 10^2		

[a] I = 0·03M. [b] I = 0·01M. [c] Values corrected for Pb^{2+}, NO_3^- association.

* β_1 in l mol^{-1}, β_2 in l^2 mol^{-2}, and β_3 in l^3 mol^{-3}.

It is probable that the ligands are bidentate in their complexes with cadmium(II) and lead(II) being linked to the metal ion by the hydrazine nitrogen atom and the oxygen (or sulphur or selenium) atom, as has been shown to be the case with complexes of zinc [9] and nickel.[19] In the case of silver(I) complexes with thiosemicarbazide and selenosemicarbazide, the ligands are probably monodentate being linked to the metal atom by the sulphur and selenium atoms. This has been shown to be true for the complex [Ag(tsc)]Cl by *X*-ray diffraction studies,[5] and indicated for [Ag$_2$(tsc)$_3$](NO$_3$)$_2$ by its i.r. spectrum,[6] and Toropova and Kirillova [7] conclude the same for [Ag(tsc)$_3^+$] because its stability is very similar to that of the analogous thiourea complex. It is probable that semicarbazide is linked to silver by the hydrazine nitrogen atom rather than the oxygen atom. We have no direct evidence of this, but the similarity of the heat of formation of the [Ag(sc)$_2$]$^+$ complex to that of [Ag(NH$_3$)$_2$]$^+$

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[16] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, 1930, **26**, 592; W. D. Bale, E. W. Davies, and C. B. Monk, *ibid.*, 1956, **52**, 816.

[17] C. J. Nyman, D. K. Roe, and R. A. Plane, *J. Amer. Chem. Soc.*, 1961, **83**, 323.

[18] G. H. Nancollas, *J. Chem. Soc.*, 1955, 1458.

[19] R. Gronbaek and S. E. Rasmussen, *Acta Chem. Scand.*, 1962, **16**, 2325.

TABLE 4

Summary of thermodynamic parameters (standard deviations in parentheses) at 30 °C and $I = 0{\cdot}1$M

		Semi-carbazide	Thiosemi-carbazide	Selenosemi-carbazide
Ag^{I} *	ΔG_{0-1}	−2·7(0·1)		
	ΔH_{0-1}	−2·2(0·5)		
	ΔS_{0-1}	+2(1)		
	ΔG_{0-2}	−3·7(0·1)	−14·6(0·2)	−18·9(0·1)
	ΔH_{0-2}	−12·5(1)	−22·0(0·3)	−28·2(0·2)
	ΔS_{0-2}	−29(4)	−24(2)	−31(1)
	ΔG_{0-3}		−17·3(0·2)	−21·6(0·1)
	ΔH_{0-3}		−27·0(0·2)	−30·8(0·1)
	ΔS_{0-3}		−32(1)	−30(1)
Cd^{II}	ΔG_{0-1}	−1·7(0·1)	−3·1(0·05)	−4·0(0·05)
	ΔH_{0-1}	−2·8(0·5)	−4·3(0·5)	−3·1(0·4)
	ΔS_{0-1}	−4(1)	−4(1)	+3(1)
	ΔG_{0-2}	−3·9(0·1)	−6·1(0·1)	−7·0(0·05)
	ΔH_{0-2}	−5·0(0·4)	−8·9(0·5)	−11·4(0·5)
	ΔS_{0-2}	−4(1)	−9(1)	−14(1)
Pb^{II}	ΔG_{0-1}	−2·9(0·1)	−2·6(0·1)	−3·1(0·1)
	ΔH_{0-1}	−3·5(0·05)	−4·2(0·05)	−4·8(0·2)
	ΔS_{0-1}	−2(1)	−5(1)	−6(1)
	ΔG_{0-2}	−3·9(0·2)		
	ΔH_{0-2}	−6·9(0·1)		
	ΔS_{0-2}	−10(1)		

ΔG, ΔH in kcal mol^{-1}, ΔS in cal K^{-1} mol^{-1}.

* For the ligands tsc and ssc, $I = 0{\cdot}03$ and $0{\cdot}01$M respectively. The subscript 0—1 refers to the reaction M → ML, 0—2 to M → ML_2 *etc.*

(ΔH −13·4 kcal mol^{-1} at 25 °C)[20] would seem to indicate bonding to the nitrogen atom in the sc complex.

Thermodynamic parameters are listed in Table 4. Silver(I) ion shows typical class ' b ' metal-ion behaviour, the free energy and enthalpy order for the donor atoms being $0 \ll S < Se$. The entropy terms are large and negative but are dominated by the large enthalpy changes. Cadmium(II) complexes with two ligand molecules and the lead(II) complexes reveal weaker class ' b ' behaviour. The enthalpy sequence is still $O < S < Se$ but the differences are less marked. The entropy changes follow the same sequence, which would tend to make the complexes less stable in going from O to Se. In fact the enthalpy change still just dominates the free-energy change for cadmium(II), resulting in the normal stability sequence $O < S < Se$, but no longer does so for lead(II) resulting in the unusual sequence $S < O < Se$. We have already discussed [1] a similar case of a borderline metal ion, copper(II), where, although the enthalpy sequence is $O < S < Se$, the stability sequence is $O < Se < S$. The cadmium(II) complexes with one ligand molecule have a normal class ' b ' stability sequence of $O < S < Se$, but the rather strange enthalpy order of $O < Se < S$. We have no explanation of this at the present time.

[2/1475 *Received*, 26*th June*, 1972]

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[20] W. V. Smith, O. L. I. Brown, and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 1213.