Ligands containing Elements of Group 6B. Part VII.[1] Comparison of the Donor Properties of some Dicarboxylic Acids of Sulphur, Selenium, and Tellurium towards Silver(I) and some Bivalent Metal Ions †

By **David K. Laing** and **Leslie D. Pettit,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The ligands $X(CH_2CH_2CO_2H)_2$ (X = O, S, Se, and Te), $Se(CH_2CO_2H)_2$, $X[CH(Me)CO_2H]_2$ (X = S or Se), and $HO_2CCH_2SCH_2CH_2CO_2H$ have been synthesised and the formation constants of their complexes with H^+, Ag^+, and a number of bivalent metal ions measured potentiometrically at 25 °C and $I = 0.10$M ($K[NO_3]$). With Ag^+ the stability order is $Te > Se > S \gg O$.

ELEMENTS of Group 6B other than oxygen are typically ' soft ' donors forming comparatively stable complexes with ' soft ' or class ' b ' acceptors such as Ag^+. In earlier papers in this series it has been shown that with sulphur(II) and selenium(II) this stability is the result of a large favourable enthalpy change on complex formation opposed by an unfavourable entropy change,[2] properties typical of ' soft–soft ' interactions.[3] A comparison of

---

† No reprints available.

[1] Part VI, G. J. Ford, P. Gans, L. D. Pettit, and C. Sherrington, *J.C.S. Dalton*, 1972, 1763.

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

[3] S. Ahrland, *Structure and Bonding*, 1973, **15**, 167.

the donor properties of sulphur with those of selenium shows that, in all cases, the silver–selenium complexes are more stable than their sulphur analogues, and that this increase in stability is the result of both favourable enthalpy and smaller unfavourable entropy changes.[2] This behaviour contrasts with the donor properties towards Ag^+ of the Group 5B analogues, phosphorus(III), arsenic(III), and antimony(III), where phosphorus forms the most stable silver complexes with stabilities decreasing towards antimony. Group 7B donors show the opposite trend, the stabilities of complexes with 'soft' acceptors falling in the order $I^- > Br^- > Cl^-$.[4] In general, Group 5 donors exist as neutral trivalent compounds of formula XR_3 whereas the halides co-ordinate as anions of formula X^-. Hence differences in the trend in donor properties are not unexpected. However, on this argument, the trend in Group 6 should be comparable to that in Group 5 rather than 7 since, in general, Group 6 ligands which have been studied are analogues of thioethers rather than thiols. Experimental evidence comparing S^{II} and Se^{II} is contrary to this simple assumption.[2,5]

Unfortunately no reliable data exist on the stabilities of complexes of tellurium(II) in solution. There are several reasons for this lack of information. Organotellurium compounds are often unpleasant to handle and the preparation of Te^{II} compounds is surprisingly difficult. The ease of disproportionation to elemental tellurium and a higher oxidation state in acid or alkaline solution necessitates carefully controlled and comparatively mild experimental conditions.

We report here the synthesis of a water-soluble ligand containing Te^{II} [3,3′-tellurodipropionic acid, $Te(CH_2CH_2CO_2H)_2$] together with its sulphur and selenium analogues, and a study of the stabilities of the complexes of these and some related diacetic acid ligands with Ag^+ and some bivalent metal ions. The ligands fall into three classes: $X(CH_2CH_2CO_2H)_2$ (X = O, S, Se, or Te); $X(CH_2CO_2H)_2$ (X = O, S, Se, with some information on Te); and $X[CH(Me)CO_2H]_2$ (X = S or Se). In addition the 'mixed' sulphur ligand, $HO_2CCH_2S(CH_2)_2CO_2H$ was also studied.

EXPERIMENTAL

Synthesis of Ligands.—Bis(2-carboxyethyl) ligands (dipropionic acids) of general formula $X(CH_2CH_2CO_2H)_2$ were prepared by treating the hydride H_2X with acrylonitrile to give the bis(2-cyanoethyl) compound, $X(CH_2CH_2CN)_2$, which was subsequently hydrolysed in acid conditions to the dicarboxylic acid. Synthesis of the 2-cyanoethyl derivatives has been reported by Kaabak who electrolysed the Group 6 element in the presence of acrylonitrile.[6] Instructions were incomplete and all attempts to reproduce the conditions were unsuccessful, probably due to difficulties in deoxygenation of the solution and the control of temperature and pH under the high current density required. A new synthesis, starting from the Group 6 hydride, was therefore devised since this was probably the intermediate through which the Kaabak synthesis proceeded. The reaction was shown to be base catalysed.

3,3′-*Tellurodipropionic acid.* Hydrogen telluride was prepared by adding aluminium telluride [prepared from tellurium (80 g) and aluminium (30 g)] in small quantities to deoxygenated hydrochloric acid (2M) * at 0 °C. The H_2Te generated was led as quickly as possible, using the minimum tube length possible, into a well stirred solution of sodium methoxide (0.1 g) in acrylonitrile (40 g) maintained at 20 °C. When all the Al_2Te_3 had been added the contents of the cyanoethylation flask were extracted with benzene, the solution filtered, washed rapidly with HCl (0.1M), and dried over anhydrous sodium sulphate. The solution was concentrated and $Te(CH_2CH_2CN)_2$ precipitated on adding light petroleum and cooling. It was recrystallised from diethyl ether as white crystals (Found: C, 30.2; H, 3.7. Calc. for $C_6H_8N_2Te$: C, 30.6; H, 3.4%), m.p. 60 °C, yield 22%. The i.r. spectrum confirmed the presence of a cyanide group.

Attempts to hydrolyse the cyanide under alkaline conditions produced coloured polytellurides. It was therefore hydrolysed by heating under reflux with HCl (6M) and cooling in ice to give white *crystals* of the required product (together with elemental tellurium). It was recrystallised from aqueous acetone (Found: C, 26.3; H, 3.6. Calc. for $C_6H_{10}O_4Te$: C, 26.3, H, 3.7%), m.p. 160 °C, yield 87%.

3,3′-*Selenodipropionic acid.* This was prepared in a similar way. Since hydrogen selenide is much more stable than H_2Te, precautions to minimise decomposition were less important and the reaction with acrylonitrile was carried out at 60 °C and H_2Se was passed until the exhaust gases precipitated cadmium selenide from an aqueous cadmium sulphate solution. The viscous $Se(CH_2CH_2CN)_2$ was extracted with benzene, washed with water, and dried over anhydrous $Na_2[SO_4]$. Benzene was removed by distillation and the remaining oil distilled *in vacuo*. On cooling to −70 °C a yellow solid was obtained and was recrystallised from acetone (Found: C, 38.8; H, 4.4. Calc. for $C_6H_8N_2Se$: C, 38.5; H, 4.3%), m.p. 48 °C, yield 95%.

The addition reaction was shown to be base catalysed. In the absence of sodium methoxide and using carefully purified acrylonitrile no $Se(CH_2CH_2CN)_2$ was formed. The use of toluene-*p*-sulphonic acid as catalyst was also unsuccessful. A similar base-catalysed reaction has been reported with hydrogen sulphide,[7] and base catalysis appeared to be essential also with H_2Te although experimental conditions were critical in the latter case and some attempts failed completely, giving no yield of the cyanide, for no identified reason.

Hydrolysis of $Se(CH_2CH_2CN)_2$ was carried out in the same way as with the telluride and the resulting 3,3′-*selenodipropionic acid* recrystallised from water (Found: C, 31.8; H, 4.4. Calc. for $C_6H_{10}O_4Se$: C, 32.0; H, 4.4%), m.p. 146—147 °C, yield 92%. 3,3′-*Thiodipropionic acid* was prepared from H_2S in a similar way and recrystallised from water (Found: C, 40.0; H, 5.6. Calc. for $C_6H_{10}O_4S$: C, 40.4; H, 5.6%), m.p. 133 °C.

3,3′-*Oxydipropionic acid.* This was prepared by heating acrylonitrile (53 g), dioxan (80 cm^3), sodium hydroxide

---

* 1M = 1 mol dm^{-3}, 1 mmHg ≈ 13.6 × 9.8 Pa.

[4] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

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

[6] L. V. Kaabak, *Zhur. Vsesoyuz Khim. obshch. im. D. T. Mendeleeva*, 1964, **9**, 700.

[7] A. Gershbein and G. Hurd, *J. Amer. Chem. Soc.*, 1947, **69**, 241.

(1 g), and water (10 cm^3) under reflux for 6 h to give $O(CH_2CH_2CN)_2$ which was purified by distillation under reduced pressure (b.p. 178 °C, at 9.5 mmHg). The cyanide was hydrolysed with HCl (10M) and the *acid* recrystallised (with difficulty) from acetone–light petroleum [8] (Found: C, 43.9; H, 5.8. Calc. for $C_6H_{10}O_5$: C, 44.4; H, 6.2%), m.p. 60 °C.

Selenodiacetic and 2,2′-selenodipropionic acids. These were prepared by methods based on that of Fredga.[9] Sodium selenide was prepared by treating reprecipitated selenium (16 g) with sodium metal (9.2 g) in liquid ammonia (200 cm^3) at −70 °C. The selenide was treated with chloroacetic or 2-bromopropionic acid in sodium hydroxide (7M) over a steam-bath for 6 h. The solution was filtered, acidified to pH 4 (further acidification led to substantial decomposition), and extracted with diethyl ether. *Selenodiacetic acid* was recrystallised from ethyl acetate (Found: C, 24.5; H, 2.95. Calc. for $C_4H_6O_4Se$: C, 24.4; H, 3.0%), m.p. 109 °C, yield 62%. *2,2′-Selenodipropionic acid* was recrystallised from acetone–benzene (Found: C, 31.9; H, 4.8. Calc. for $C_6H_{10}O_4Se$: C, 32.0; H, 4.5%), m.p. 120—121 °C, yield 6%. *2,2′-Thiodipropionic acid* was prepared in a similar way from sodium sulphide (Found: C, 40.4; H, 5.6. Calc. for $C_6H_{10}S$: C, 40.5; H, 5.6%), m.p. 98—99 °C.

(3-Carboxymethylthio)propionic acid. This was prepared by treating thioglycolic acid methyl ester (24 g) with acrylonitrile (25 g) in the presence of Na(OMe) (0.1 g) at 45 °C. The resulting cyanide was purified by distillation under reduced pressure and hydrolysed by heating under reflux for 3 h with NaOH solution (8M). The solution was acidified to pH 3 and extracted with diethyl ether and the product recrystallised from acetone–petroleum (Found: C, 35.9; H, 4.9. Calc. for $C_5H_8O_4S$: C, 36.5; H, 4.9%), m.p. 92 °C, yield 83%.

Tellurodiacetic acid. This compound was reported by Morgan and Drew [10] but attempts to repeat the preparation always failed. Bis(carboxymethyl)tellurium dichloride was prepared from $TeCl_4$, acetic anhydride, and chloroform, but all attempts at reduction caused an immediate blackening. Early attempts in this laboratory to reduce the Te^{IV} compound gave an impure product which was titrated and shown to be *ca.* 80% $Te(CH_2CO_2H)_2$.[11] Approximate acid-association constants were calculated but metal complexes were not studied because of decomposition. Attempts to reduce the Te^{IV} using sodium hydrogensulphite, sodium dithionite, tin(II) chloride, iron(II) sulphate, hydrazine, or electrolysis all failed to effect reduction in alkaline solutions or yielded tellurium metal under acid conditions. When two equivalents of reducing agent were used per mol of dichlorotellurium compound almost equal quantities of tellurium and hydrolysed starting material were recovered, suggesting that the disproportionation reaction $2Te^{II} \longrightarrow Te^0 + Te^{IV}$ was taking place comparatively rapidly.

Complex-formation Constants.—These were measured potentiometrically at 25 °C and $I = 0.10$M-K[NO$_3$] using a glass electrode calibrated in terms of hydrogen-ion concentrations.[12] In the presence of Ag^+, constants were also measured by following changes in silver activity with a silver(I) halide electrode in buffer solutions of pH 1.55 and 5.95 and an ionic strength of 0.20M (acetate).[5] Formation constants were calculated from the experimental data with the aid of the Miniquad computer program.[13]

RESULTS AND DISCUSSION

Hydrogen-ion complex-formation constants (acid-association constants) are in Table 1. For comparable ligands, the values for both K_{HL} and K_{H_2L} fell in the order O < S < Se < Te < CH_2, in accordance with decreasing electronegativity of the Group 6 atoms going down the Group. For a particular Group 6 donor atom the order of formation constants as the substituent group is varied, acetic < 2-propionic < 3-propionic, is expected from the inductive effects of the substituents. The ratio of the stepwise constants approached the statistically expected value of 4 in the 3-propionic acids but is considerably larger when the carboxyl groups are less independent of one another. Complex-formation constants with bivalent metal ions are in Table 2. Under the conditions used (metal : ligand = 1 : 1) both [M(HL)] and [ML] complexes were important but the [ML$_2$] species was insignificant. In many cases the complexes were comparatively weak and ill defined. The errors quoted refer only to random errors and systematic errors could assume importance in such small constants. However the constants quoted are of value for comparison purposes.

TABLE 1

Hydrogen-ion complex-formation constants at 25 °C and $I = 0.10$M (K[NO$_3$]). Standard deviations are given in parentheses

Ligand (H_2L)	log K_{HL}	log $K_{H_2L}{}^{HL}$	$K_{HL} : K_{H_2L}$
$O(CH_2CH_2CO_2H)_2$	4.624(2)	3.770(2)	7.2
$S(CH_2CH_2CO_2H)_2$	4.672(2)	3.901(2)	5.9
$Se(CH_2CH_2CO_2H)_2$	4.702(2)	3.896(2)	6.4
$Te(CH_2CH_2CO_2H)_2$	4.767(2)	3.924(2)	7.0
$CH_2(CH_2CH_2CO_2H)_2$	5.053(1)	4.316(1)	5.4
$O(CH_2CO_2H)_2$	4.11 [a]	3.06 [a]	12.7
$S(CH_2CO_2H)_2$	4.19 [b]	3.25 [b]	8.7
$Se(CH_2CO_2H)_2$	4.345(2)	3.266(2)	12.0
$Te(CH_2CO_2H)_2$	4.77 [c]	3.26 [c]	32.4
$CH_2(CH_2CO_2H)_2$	5.01 [d]	4.14 [d]	7.4
$S[CH(Me)CO_2H]_2$	4.192(2)	3.117(2)	11.9
$Se[CH(Me)CO_2H]_2$	4.658(2)	3.351(2)	20.3
$HO_2CCH_2SCH_2CH_2CO_2H$	4.336(3)	3.272(2)	11.6

[a] E. Camp, G. Ostacoli, N. Cibrario, and G. Saini, *Gazetta*, 1961, **91**, 361. [b] M. Yasuda, K. Yamasaki, and H. Ohtaki, *Bull. Chem. Soc. Japan*, 1960, **33**, 1067. [c] Ref. 11. [d] K. Suzuki and K. Yamasaki, *Bull. Chem. Soc. Japan*, 1959, **32**, 982.

The question of co-ordination between the Group 6 donor centre and the bivalent metal ion is particularly important. It can be best examined by comparing values for log K_{ML} − log β_{H_2L} to allow for variations in the donor properties of the carboxyl groups resulting from differing electronegativities of the Group 6 atoms. In all cases the values suggest that bonding by the Group 6 donor is significant as illustrated in the Figure where

---

[8] R. V. Christian and R. M. Hixon, *J. Amer. Chem. Soc.*, 1948, **70**, 1333.

[9] A. Fredga, *Upsaala Univ. Arsskrift*, 1935, **5**, 1.

[10] J. F. Morgan and L. Drew, *J. Chem. Soc.*, 1925, 531.

[11] D. S. Barnes, personal communication.

[12] M. Israeli, D. K. Laing, and L. D. Pettit, *J.C.S. Dalton*, 1974, 2194.

[13] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

TABLE 2

Metal-complex formation constants at 25 °C and $I = 0.10\text{M}$ (K[NO$_3$])

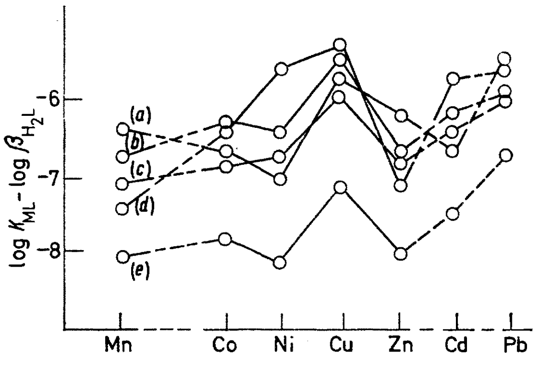
Ligand (H_2L)	Complex species	log K_{ML} or log $K_{M(HL)}{}^{HL}$ values						
		Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
$O(CH_2CH_2CO_2H)_2$	[ML]	2.0(1)	1.69(4)	1.39(4)	2.52(8)	2.13(6)	1.66(1)	2.66(1)
	[M(HL)]				1.4(1)			1.73(5)
$S(CH_2CH_2CO_2H)_2$	[ML]	1.77(3)	2.25(1)	2.15(1)	2.97(1)	1.72(2)	2.31(1)	2.57(1)
	[M(HL)]		1.87(3)	1.76(6)	1.80(2)	1.28(3)	1.77(1)	1.82(3)
$Se(CH_2CH_2CO_2H)_2$	[ML]	1.50(4)	1.82(2)	1.83(4)	2.60(1)	1.77(1)	2.07(1)	2.58(1)
	[M(HL)]		1.43(5)	1.56(3)	1.59(4)	1.05(8)	1.52(4)	1.95(3)
$Te(CH_2CH_2CO_2H)_2$	[ML]	1.2(1)	2.36(5)	3.0(1)	3.2(1)	1.4(1)	2.85(5)	2.94(5)
	[M(HL)]		1.9(1)	2.8(1)	2.7(2)		2.4(1)	2.3(2)
$CH_2(CH_2CH_2CO_2H)_2$	[ML]	1.33(2)	1.50(1)	1.20(3)	2.21(1)	1.3(1)	1.76(1)	2.62(1)
$Se(CH_2CO_2H)_2$	[ML]	2.02(1)	2.47(1)	2.96(1)	3.55(1)	2.18(1)	2.57(1)	3.22(1)
	[M(HL)]	0.88(8)	1.37(6)	1.76(1)	2.50(1)	1.05(8)	1.82(1)	2.16(2)
$S[CH(Me)CO_2H]_2$	[ML]	2.1(1)	3.14(1)	3.59(1)	3.97(1)	2.13(2)	2.25(1)	3.12(1)
	[M(HL)]		2.2(1)	1.7(1)	1.8(1)			1.8(1)
$Se[CH(Me)CO_2H]_2$	[ML]	2.02(1)	2.20(1)	2.73(3)	3.21(1)	1.80(2)	2.09(1)	2.80(2)
	[M(HL)]		1.1(1)	1.8(1)	2.1(1)		0.9(1)	1.7(1)
$HO_2CCH_2SCH_2CH_2CO_2H$	[ML]	1.70(3)	2.11(2)	2.30(2)	3.75(1)	1.70(3)	3.09(3)	3.59(4)
	[M(HL)]				1.5(1)		1.05(6)	2.01(1)

TABLE 3

Silver complex formation constants at 25 °C and (*a*) 0.10M-K[NO$_3$] (pH titration) or (*b*) 0.20M-acetate buffer (pH 1.55 or 5.95)

Ligand (H_2L)		log K_{AgL}	log $K_{AgL_2}{}^{AgL}$	log $K_{Ag(HL)}{}^{HL}$	log $K_{Ag(H_2L)}{}^{H_2L}$	log $K_{Ag(H_2L)_2}{}^{Ag(H_2L)}$
$S(CH_2CH_2CO_2H)$	(*a*)	3.85(8)		3.34(1)	3.22(1)	
	(*b*)	3.95(1)	2.53(2)		3.18(1)	2.41(4)
$Se(CH_2CH_2CO_2H)$	(*a*)	4.5(2)?		4.32(1)	3.96(1)	
	(*b*)	4.97(3)	2.39(6)		4.05(1)	1.57(5)
$Te(CH_2CH_2CO_2H)_2$	(*a*)	?		5.35(1)	4.97(1)	
	(*b*)	6.28(1)	2.90(5)		5.03(1)	2.74(2)
$S(CH_2CO_2H)_2$	(*a*)	4.04(1)		3.06(1)	2.35(4)	
$Se(CH_2CO_2H)_2$	(*a*)	4.46(1)		3.42(1)	3.02(1)	
	(*b*)	4.20(1)	2.56(2)		2.77(2)	1.84(4)
$S[CH(Me)CO_2H]_2$	(*a*)	?		3.15(1)	2.74(1)	
	(*b*)	3.81(2)	2.21(3)		2.81(1)	1.51(1)
$Se[CH(Me)CO_2H]_2$	(*a*)	?		3.72(1)	3.01(1)	
	(*b*)	4.55(1)	2.37(4)		2.90(3)	1.88(5)
$HO_2CCH_2SCH_2CH_2CO_2H$	(*a*)	3.9(1)?		3.63(1)	3.41(2)	
	(*b*)	4.40(1)	3.06(5)		3.50(1)	2.51(6)

the curve for the ligand in which the methylene group replaces the Group 6 atom is *ca.* 1 log unit lower than for all the other ligands. In addition the high stability of the protonated complexes, [M(HL)], supports chelate formation through the Group 6 donor atom. In general the complexes are weak and, for this reason, many poorly defined constants have been omitted from the Table. As a result of the low values the absolute accuracy of the constants is low so that detailed interpretation of the Figure is not reliable. However, the general trend among the first-row transition elements (the Irving–Williams order) is clear. Curves similar to those in the Figure were obtained by comparing the diacetic acids or the ligands containing sulphur and those containing selenium.



Co-ordination between bivalent metal ions and Group 6 donor atoms, X, in $X(CH_2CH_2CO_2H)_2$. X = O (*a*), S (*b*), Se (*c*), Te (*d*), and CH_2 (*e*)

The only significant deviation from expected behaviour was the generally low values for the formation constants of the complexes with Ni^{2+}, where the Irving–Williams order predicts a stability greater than that for the complexes with Co^{2+}. This behaviour has been noticed previously in a number of studies of complexes containing sulphur-donor atoms.[1,14] This anomalous behaviour of Ni^{2+} is independent of the methods of measurement since various workers have used pH titrations, nickel(II)-specific electrodes, and competition with Ag^+ at a silver(I) halide electrode. One possible explanation is a

---

[14] K. Suzuki and K. Yamasaki, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1093; G. Schwarzenbach and G. Senn, *Helv. Chim. Acta*, 1955, **38**, 1147; A. Sandell, Dissertation, Lund, 1971.

change from octahedral to tetrahedral co-ordination in the presence of the heavier donor atoms but this is unlikely, particularly in aqueous solutions with ligands exerting little steric interference. Possible binuclear-complex formation was considered and attempts were made to fit various models including species such as $[Ni_2L_2]$ to the experimental data. Their inclusion produced only a marginal improvement in the statistical fit and hardly affected the values for K_{NiL} or $K_{Ni(HL)}$, the polymeric species always being only very minor components of the equilibrium mixture. They were therefore ignored.

Silver complex-formation constants are in Table 3. These were measured by two different methods. pH Titrations in 0.10M-$K[NO_3]$ solutions of 1 : 1 ligand–silver(I) mixtures showed the presence of the complexes [Ag(HL)] and $[Ag(H_2L)]^+$. The unprotonated complex, $[AgL]^-$, was also detected with reasonable certainty with some ligands but, in general, the pH values used to avoid precipitation were too low to give meaningful results. Titrations were also made by adding ligand solution to Ag^+ in acetate buffer solutions of pH 1.55 and 5.95 ($I =$ 0.20M). By using large L : Ag ratios the complex species [AgL], $[AgL_2]$, $[Ag(H_2L)]$, and $[Ag(H_2L)_2]$ were detected, although at pH 5.95 allowance had to be made for the presence of [Ag(HL)] species. Constants measured in the different media were in reasonable agreement (Table 3). The ligands $O(CH_2CH_2CO_2H)_2$ and $CH_2(CH_2CH_2CO_2H)_2$ did not form complexes of sufficient stability to give meaningful formation constants.

It is assumed that, in all the complex species, bonding is almost exclusively through the Group 6 donor atom with minimal chelation through the carboxyl groups. This is supported by the small differences between the formation constants for the [AgL], [Ag(HL)], and $[Ag(H_2L)]$ complexes, by the apparent absence of silver complexes of the methylene analogue, and the similarity between the constants measured in nitrate and acetate media. The general trend in formation constants was Te > Se > S ⩾ O, behaviour typical of soft–soft interactions. The complexes with tellurium were significantly more stable than those with selenium, showing a closer resemblance to Group 7 donors than Group 5. Complexes with the 3-propionic acids were more stable than their acetic acid analogues, as expected if the carboxyl groups are non-co-ordinating.

The ratio of stepwise formation constants, $K_{ML} : K_{ML_2}$, has been interpreted by Ahrland *et al.*[15] as evidence of the presence or absence of d–d_π bonding. It is interesting to note that this ratio increases in the order S < Se < Te, and $L^{2-} > H_2L$ for a particular ligand. If a large value for $K_{ML} : K_{ML_2}$ (*i.e.* greater than 10^2) indicates significant π bonding, it is probably absent in the sulphur ligands (ratio 10—100 : 1), weak with the selenium, and significant with the tellurium ligand (ratio 2 400 : 1).

An attempt was made to calculate enthalpy and entropy charges accompanying complex formation by carrying out the titrations at a range of temperature between 0 and 40 °C. Titrations were made in the nitrate medium with the result that only the species [Ag(HL)] and $[Ag(H_2L)]$ were formed in acceptable concentrations. Constants calculated at 1.7, 25, and 38 °C allowed calculation of values of ΔH and $T\Delta S$ (Table 4). Unfortunately the precision of these values is low but the trend in $-\Delta H$ is similar to that in $-\Delta G$, *i.e.* Te > Se > S, suggesting an increase in the covalent character of the silver–donor bond as the donor atom increases in size.

TABLE 4

Thermodynamic data (kJ mol^{-1}) for complexes of some Group 6 donors with Ag^+ in 0.10M-$K[NO_3]$ at 25 °C. Standard deviation are given in parentheses

Ligand (H_2L)	Species	$-\Delta H$	$-\Delta G$	$-T\Delta S$
$S(CH_2CH_2CO_2H)_2$	[Ag(HL)]	26(3)	19.1(1)	7(3)
	$[Ag(H_2L)]$	22(2)	18.4(1)	4(2)
$Se(CH_2CH_2CO_2H)_2$	[Ag(HL)]	31(6)	24.7(1)	6(6)
	$[Ag(H_2L)]$	30(5)	22.6(1)	7(5)
$Te(CH_2CH_2CO_2H)_2$	[Ag(HL)]	33(8)	30.6(1)	2(8)
	$[Ag(H_2L)]$	32(5)	28.4(1)	4(5)

[5/740 *Received*, 21*st April*, 1975]

---

[15] S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 1958, 264, 276.