Co-ordination of Silver(I) to Olefinic Bonds. Complex Formation between Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II), and Silver(I) and some Unsaturated Derivatives of Acetic and Iminodiacetic Acids

By **Mordecai Israeli** and **Leslie D. Pettit**,* Department of Inorganic and Structural Chemistry, The University, Leeds L2S 9JT

A number of substituted malonic, $RCH(CO_2H)_2$, acetic, RCH_2CO_2H, and iminodiacetic acids, $RN(CH_2CO_2H)_2$, containing substituent groups incorporating olefinic bonds have been synthesised ($R = CH_2{:}CH{\cdot}CH_2$, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$, and $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$) and the formation constants of their complexes with H^+, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ag^+ measured at 25 °C and $I = 0{\cdot}10$M. Chelate formation takes place between the Ag^+ ion and the ligands able to form chelate rings which are 'four-and-a-half' membered or larger. There is no evidence for chelate formation with the other metal ions studied. Potentiometric measurements over a range of temperatures show formation of the Ag^+–allylacetate mono complex to be the result of a large favourable enthalpy change ($-17{\cdot}5$ kJ mol^{-1}) opposed by the entropy change ($T\Delta S = -6{\cdot}0$ kJ mol^{-1} at 25 °C).

COMPLEX formation between the Ag^+ ion and olefinic bonds is well known. However, in aqueous solution, the complexes tend to have comparatively low stabilities and few systems have been studied quantitatively.[1] Typical of the formation constants found are those for the silver complexes of $CH_2{:}CH{\cdot}CH_2{\cdot}NH_3^+$ and $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, reported as $\log K = 0{\cdot}11$ and $1{\cdot}36$ respectively, making them comparable in stability to the fluoride or acetate complexes.[2] The stabilities are enhanced considerably if the Ag^+–olefin bond is part of a chelate ring in which the other bond is from Ag^+ to another 'soft' donor centre such as sulphur, selenium,[3] or the nitrogen atom of a pyridine ring.[4] For example, formation constants for Ag^+ complexes of $CH_2{:}CH(CH_2)_2{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$ and $Me(CH_2)_3{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$ (HL) are $\log K_{Ag(HL)} = 4{\cdot}74$ and $3{\cdot}81$ and $\log K_{AgL} = 5{\cdot}16$ and $4{\cdot}58$ respectively.[3] Chelate formation was found to be most marked when the ring so formed was 'five-and-one-half' membered. Formation of a silver–olefin bond is characterised by a large negative enthalpy change opposed by a large negative entropy change.[3,5]

Straightforward silver–acetate complex formation is weak (comparable to silver–olefin co-ordination) and there is little evidence for marked chelate formation through the carboxy-groups in thio- and seleno-acetic acids. For example, the difference between corresponding K_{AgL} and $K_{Ag(HL)}$ values is small,[3] and can be accounted for by the greater inductive effect of CO_2^- compared to CO_2H. Hence it appears that while soft-donor centres such as sulphur and selenium encourage Ag^+–olefin co-ordination, they do not similarly encourage $Ag^+{-}O_2CCH_2$ bonding (an example of a *symbiotic* effect). The extent of chelate formation between Ag^+ and an olefinic bond and a carboxy-group is therefore of interest.

To this end we have synthesised two series of aliphatic carboxylic acids with side chains containing olefinic groups able to form chelate rings of varying size and measured the formation constants of their complexes with the hydrogen ion, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Ag^+. The corresponding carboxylic acids containing the fully saturated butyl side chain were studied for comparison. The series of ligands selected were substituted alkylmalonic acids, $RCH(CO_2H)_2$, and alkylacetic acids, RCH_2CO_2H (R = allyl, but-1-enyl, pent-1-enyl-, and butyl). In addition, the formation of silver complexes of allylacetic acid as a function of temperature was studied to give the enthalpy change accompanying the reaction. A third series of ligands, *N*-substituted iminodiacetic acids $RN(CH_2CO_2H)_2$, should give information on chelate formation between an aliphatic nitrogen donor and an olefinic bond in the substituent group R. However ligands giving a suitably sized chelate ring could not be readily prepared. Results obtained for a limited range are included.

EXPERIMENTAL

Preparation of Ligands.—Alkylmalonic acids were prepared by adding the alkyl bromide dropwise with cooling to a solution of sodium diethylmalonate in ethanol.[6] The mixture was heated under reflux for 10 h and the product was poured into calcium chloride solution and extracted with diethyl ether. The ether was removed by distillation and the mixture hydrolysed overnight with a solution of

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[1] L. D. Pettit and D. S. Barnes, *Topics Current Chem.*, 1972, **28**, 85.

[2] F. R. Hartley and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 333.

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

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

[5] S. Ahrland, *Structure and Bonding*, 1968, **5**, 118; 1973, **15**, 167.

[6] P. Gaubert, R. P. Linstead, and H. N. Rydon, *J. Chem. Soc.*, 1937, 1971.

potassium hydroxide in aqueous alcohol. The resulting solution was concentrated *in vacuo*, acidified with hydrochloric acid to pH 1 (Congo Red), and extracted with diethyl ether. After evaporation to dryness, the acids were recrystallised from benzene–light petroleum to give white crystals.

Alkylacetic acids were obtained by decarboxylating the corresponding malonic acids at 160 °C for 24 h. The cooled product was leached out with aqueous sodium hydrogencarbonate solution and neutral by-products removed by extraction with diethyl ether. The aqueous solution was then acidified with hydrochloric acid and extracted with diethyl ether. The alkylacetic acids were purified by fractional distillation.

TABLE 1

Analytical data for the ligands

Ligand	R	M.p. (θ_c/°C)	Analyses */% C	H	N
$RCH(CO_2H)_2$	$CH_2{:}CH{\cdot}CH_2$	134	50·2 (50·0)	5·75 (5·6)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$	88	53·3 (53·2)	6·25 (6·35)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2CH_2$	99	55·8 (55·8)	7·0 (7·0)	
	Bu^n	110	52·5 (52·5)	7·35 (7·5)	
RCH_2CO_2H	$CH_2{:}CH{\cdot}CH_2$	188—189 †	60·0 (60·1)	7·8 (8·0)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$	108 (15 mmHg) †	63·3 (63·2)	8·8 (8·8)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	125 (15 mmHg) †	66·8 (66·6)	9·55 (9·35)	
$RN(CH_2CO_2H)_2$	$CH_2{:}CH{\cdot}CH_2$	178	48·6 (48·6)	6·25 (6·4)	8·1 (8·1)
	$MeCH_2{\cdot}CH_2$	174	48·2 (48·0)	7·35 (7·5)	7·7 (8·0)
	$MeCH_2{\cdot}CH_2{\cdot}CH_2$	186	50·8 (50·8)	8·05 (8·0)	7·6 (7·4)
	$PhCH_2$	206	59·0 (59·2)	5·85 (5·85)	6·2 (6·3)
	$2\text{-}C_5H_4N{\cdot}CH_2(\tfrac{1}{2}H_2O)$	183	51·3 (51·5)	5·6 (5·6)	12·0 (12·0)
$(CH_2{:}CH{\cdot}CH_2)_2N(CH_2CO_2H)_2$		>200 (decomp.)	56·5 (56·4)	7·35 (7·1)	6·9 (6·6)

* Calculated values are given in parentheses. † B.p.

N-Substituted iminodiacetic acids were prepared by a method based on that of Blatt.[7] The amine RNH_2 was added slowly to an alkaline aqueous solution of sodium chloroacetate in such a way that the temperature did not exceed 50 °C. The barium salt of the iminodiacetic acid was precipitated, coagulated by heating on a steam-bath for 2 h, and filtered off. The barium salt was dissolved in water, treated with sulphuric acid to remove the barium, and the solution evaporated to dryness under reduced pressure. The syrupy product was recrystallised from methanol, often with difficulty. An attempt to prepare diallylaminoacetic acid by using a large excess of diallylamine failed, the zwitterion diallyliminodiacetate being formed.

The properties of the ligands prepared are given in Table 1.

Measurement of Protonation and Complex-formation Constants.—For the hydrogen ion and all metal ions other than Ag^+, formation constants were calculated from potentiometric-titration curves as described previously.[4] In the presence of Ag^+, titrations of the malonic and acetic acids were carried out in buffer solutions at pH 1·55 and 5·95 as described previously.[4] No evidence was found for complex formation in the solution of low pH, showing the unimportance of protonated complex species. At pH 5·95 maximum silver : ligand ratios of 1 : 10 were used and even at this high ligand ratio no complexes above the simple [AgL] species could be detected. Since at pH 5·95 the ligands were often partly protonated, allowance was made for this in the calculations.

As a result of the greater basicity of the iminodiacetic acids, titrations in buffer solutions were not suitable. Silver complex-formation constants were therefore calculated from titrations of the ligands in the presence of Ag^+ with alkali, measuring both pH and pAg simultaneously. Silver : ligand ratios of 1 : 1 and 1 : 2 were used. Excellent agreement was found for values of β_{AgL} ($< \pm 0{\cdot}01$ log units). However the errors in values for β_{AgL_2} were somewhat larger since the percentage of the bis complex was always small.

RESULTS AND DISCUSSION

Calculated formation constants for protonation and the silver complexes are given in Table 2 and for complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} in Table 3. The absence of a value signifies that the complex species were too weak to give meaningful results. The protonation constants followed the pattern expected from the varying inductive effects of the substituent groups. In general, the ligands with olefinic groups in their side chains were the stronger acids, the acidity decreasing as the olefinic bond is displaced further from the carboxyl group. Assuming a linear free-energy relation between the protonation constants and the Taft σ^* functions for the substituents, Taft values for the but-1-enyl and pent-1-enyl groups were found to be −0·04 and −0·09 respectively. The ratio of the constants for the dibasic substituted malonic acids (expressed as $\Delta\log K$ for the stepwise constants) was constant ($2{\cdot}60 \pm 0{\cdot}01$) and independent of the substituent group.

The same general trend was found in the protonation constants for the nitrogen atom in the iminodiacetic acids as for the carboxyl groups. Protonation of both carboxyl groups (to give the cationic species H_3L^+) is difficult, hence the lower precision in the constants quoted. 2-Pyridylmethyliminodiacetic acid has been studied previously.[8] Protonation of the pyridine nitrogen atom appears to take place simultaneously with protonation of the first carboxyl group to give stepwise constants of 2·74 and 2·65. These are clearly macroconstants covering both protonation reactions. As expected, the benzyl and 2-pyridylmethyl groups reduce the donor power of the nitrogen atom in the ligands containing them as substituents considerably.

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[7] A. H. Blatt, *Org. Synth.*, 1974, collective vol. 2, 397.

[8] H. M. N. H. Irving and J. J. Da Silva, *J. Chem. Soc.*, 1963, 945, 1144.

Formation constants for the complexes with the bivalent metal ions studied also showed the expected trends, being directly comparable with the protonation constants with the exception of 2-pyridylmethyliminodiacetic acid in which chelate formation is clearly present. The degree of formation ($\bar{n}$) of the alkylmalonic acid complexes generally reached 0·4—0·8, while with the alkylacetic acids the values for the copper complexes did not exceed 0·2 and were considerably lower with the other bivalent metal ions. The complexes of substituted iminodiacetic acids were markedly more stable, $\bar{n}$ values reaching up to 1·8, and gave formation constants comparable with those previously reported for similar substituents.[9] The results for 2-pyridylmethyliminodiacetic acid, however, showed less satisfactory agreement with those of Irving and Da Silva [8] for the complexes with Co^{2+}, Zn^{2+}, and Cd^{2+}. There are no values in the literature for the complexes with Ni^{2+} or Cu^{2+}.

Although 2-pyridylmethyliminodiacetic acid is markedly less basic than any of the other substituted iminodiacetate ions studied, the results show that, with the exception of the complexes with Cu^{2+}, the metal complexes are more stable. This finds a ready explanation in the formation of an additional chelate ring between the metal ion and the nitrogen donor atom of the pyridine ring. In contrast to the other bivalent metal ions studied, Cu^{2+} has a preferred co-ordination number of four (square planar). For this reason the Cu–O bonds in the simple iminodiacetic acid complexes have to be strained considerably (or broken) if the pyridine nitrogen atom is to co-ordinate. Hence the enhancement in stability found with most bivalent metal ions is not found with Cu^{2+}.

TABLE 2

Protonation and silver complex-formation constants at 25 °C and I = 0·10M (KNO_3 for protonation, acetate for silver complexes) (Standard deviations, σ, are given in parentheses.)

Ligand	R	log β: HL	H_2L	H_3L	[AgL]	$[AgL_2]$
$RCH(CO_2H)_2$ (H_2L)	$CH_2{:}CH{\cdot}CH_2$	5·242 (3)	7·875 (4)		2·086 (6)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$	5·351 (5)	8·087 (6)		2·280 (5)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	5·372 (5)	8·139 (7)		2·343 (6)	
	Bu^n	5·383 (4)	5·180 (7)		0·74 (1)	
RCH_2CO_2H (HL)	$CH_2{:}CH{\cdot}CH_2$	4·451 (3)			2·009 (3)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$	4·566 (3)			2·057 (8)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	4·572 (3)			2·075 (5)	
	Bu^n	4·600 (4)				
$RN(CH_2CO_2H)_2$ (H_2L)	$CH_2{:}CH{\cdot}CH_2$	9·14 (1)	11·35 (2)	12·93 (7)	4·71 (1)	6·9 (1)
	$MeCH_2{\cdot}CH_2$	10·03 (1)	12·27 (1)	13·4 (1)	4·29 (1)	7·5 (1)
	$MeCH_2{\cdot}CH_2{\cdot}CH_2$	10·07 (1)	12·35 (1)	13·70 (6)	4·36 (1)	7·6 (1)
	$PhCH_2$	8·87 (1)	11·06 (1)	12·1 (1)	4·31 (1)	7·1 (1)
	$2\text{-}C_5H_4N{\cdot}CH_2$	8·16 (1)	10·90 (1)	13·55 (5)	6·03 (1)	9·5 (1)
		8·25 *	11·10 *		6·09 *	
$(CH_2{:}CH{\cdot}CH_2)_2N(CH_2CO_2H)_2$ (L)		2·23 (1)				

* Ref. 8, 20 °C, I = 0·1M.

TABLE 3

Formation constants for bivalent metal-ion complexes at 25 °C and I = 0·10M (KNO_3) (Standard deviations, σ, are given in parentheses.)

Ligand	R	log β: [CuL]	$[CuL_3]$	[NiL]	$[NiL_2]$	[ZnL]	$[ZnL_2]$	[CoL]	$[CoL_2]$	[CdL]	$[CdL_2]$
$RCH(CO_2H)_2$ (H_2L)	$CH_2{:}CH{\cdot}CH_2$	4·66 (2)		2·46 (4)		2·45 (2)		2·29 (3)		2·32 (2)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$	4·74 (2)		2·48 (3)		2·62 (2)		2·32 (3)		2·39 (3)	
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	4·83 (3)		2·48 (3)		2·68 (1)		2·54 (2)		2·60 (3)	
	Bu^n	4·88 (2)		2·66 (2)		2·73 (2)		2·57 (2)		2·66 (3)	
RCH_2CO_2H (HL)	$CH_2{:}CH{\cdot}CH_2$	1·42 (3)									
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2$	1·45 (3)									
	$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	1·47 (4)									
	Bu^n	1·51 (2)									
$RN(CH_2CO_2H)_2$ (H_2L)	$CH_2{:}CH{\cdot}CH_2$	10·31 (2)	18·67 (1)	8·58 (1)	15·39 (1)	7·62 (1)	14·01 (1)	7·52 (1)	13·45 (1)	5·76 (1)	12·20 (1)
	$MeCH_2{\cdot}CH_2$	11·30 (2)	19·95 (2)	8·78 (2)	15·65 (1)	8·00 (1)	14·55 (1)	7·40 (1)	13·81 (1)	6·97 (1)	12·54 (1)
	$MeCH_2{\cdot}CH_2{\cdot}CH_2$	11·31 (1)	20·04 (1)	8·84 (1)	15·88 (1)	8·12 (1)	14·88 (1)	7·71 (1)	13·78 (1)	6·98 (1)	12·63 (1)
	$PhCH_2$	10·42 (2)	19·97 (1)	7·83 (1)	13·93 (1)	6·98 (1)	12·51 (1)	6·78 (1)	12·10 (1)	6·16 (1)	11·22 (1)
	$2\text{-}C_5H_4N{\cdot}CH_2$	9·23 (1)	16·38 (1)	9·11 (2)	15·94 (3)	8·78 (1)	15·61 (1)	8·86 (1)	15·42 (4)	8·62 (2)	15·72 (3)

Formation constants of the silver complexes showed clearly the presence of chelate formation between the olefin bond and the silver ion. Unidentate silver–olefin co-ordination was not apparent since there was no detectable formation of protonated complexes in the acetate buffers used. This is to be expected if the unidentate olefin complex is of comparable stability to the very weak acetate complexes formed (log β_{AgL} 0·06).[10] When chelate formation is possible the stabilities of the complexes formed increased when the chelate ring increased from ‘ four-and-a-half ’ to ‘ five-and-a-

[9] G. Schwarzenbach, G. Anderegg, W. S. Schneider, and H. Senn, *Helv. Chim. Acta*, 1955, **38**, 1147; S. Chaberek and A. E. Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5052.

[10] F. H. McDougall and L. E. Topel, *J. Phys. Chem.*, 1952, **56**, 1090.

half ’ membered, *i.e.* on changing the substituent R from allyl to but-1-enyl, and remained effectively constant on increasing the ring size further in the pent-1-enyl substituted ligands. In allyliminodiacetic acid the N–Ag^+–olefin chelate ring would be only ‘ three-and-a-half ’ membered. This would be a very strained ring and the results gave no indication whatsoever of its formation. With the alkyl-malonic and -acetic acids effective formation of a chelate ring involving Ag^+–olefin bonding increased the stability of the complexes markedly to give extremely well defined mono complexes with no apparent formation of bis species under the conditions used. The stability of the silver–2-pyridylmethyliminodiacetic acid complexes was enhanced considerably compared to the analogues with non-bonding substituents. The value found for log β_{AgL} is very close to that reported by Irving and Da Silva[8] and there was clear evidence of a bis complex, $[AgL_2]$.

The free-energy change on complex formation between the simplest olefinic acetic acid (allylacetic acid) and Ag^+ was divided into its enthalpy and entropy components by carrying out the titrations over the temperature range 2—38 °C. The mono-complex was well defined at all the temperatures used and gave constants of high precision. To confirm the assumption that the use of an acetate buffer to maintain an effectively constant pH would not unduly affect the constants calculated, titrations were also carried out in a nitrate background, adjusting the pH to 5·95 for each datum point. Calculated constants differed by a maximum of 0·02 log units. Plots of log β_{AgL} against $(T/K)^{-1}$ produced a good straight line and the enthalpy change was calculated from the gradient $(-\Delta H/2{\cdot}303R)$. Formation constants calculated at the various temperatures, together with calculated values for ΔH and $T\Delta S$, are given in Table 4. These results confirm the expected large enthalpy contribution to the free energy of complex formation, opposed by the entropy change causing a large negative temperature coefficient in the log β values.

TABLE 4

Thermodynamic quantities for formation of the silver–allylacetate mono complex (I = 0·10M, acetate)

T/K	log β_{AgL}	$-\Delta G$/ kJ mol^{-1}	$-\Delta H$/ kJ mol^{-1}	$-T\Delta S$/ kJ mol^{-1}
275·3	2·273 (6)	11·97	17·5 (3)	5·5
293·3	2·062 (3)	11·57		5·9
298·2	2·009 (3)	11·46		6·0
311·4	1·884 (3)	11·22		6·3

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