Thermochimica Acta, 90 (1985) 1-8
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

THERMOCHEMISTRY FOR THE FORMATION OF CYSTEINATE COMPLEX OF RHODIUM(III)

C.L. SHARMA * and S.S. NARVI

Department of Chemistry, University of Roorkee, Roorkee 247 667 (India)

(Received 22 January 1985)

ABSTRACT

The stepwise formation constants, enthalpy and entropy changes for the formation of triscysteinato-Rh(III) chelate have been determined. A comparative study with α-alanine and 2-mercaptopropanoic acid confirmed the coordination of Rh(III) through the carboxyl and sulphydril groups of cysteine. The complex could be isolated in the pure form and characterised on the basis of elemental and thermal analyses, conductance, magnetic, infrared and electronic spectral studies. The complex was assigned an octahedral structure.

INTRODUCTION

A survey of the existing literature on the metal chelates of cysteine, an amino acid of biochemical importance, indicated the coordination of iron(II) and cobalt(III) through sulphydril and carboxyl groups [1-4] and of nickel(II) and lanthanide(III) ions through amino and carboxyl groups [5,6]. The enthalpy of reaction for the formation of a metal chelate in solution is the sum of the heats of formation of each of the metal-donor bonds formed. Although considerable information is available on the bonds of first-series transition metal ions with nitrogen and oxygen [7-10], very little has been done on the thermochemistry of amino-acid chelates of platinum metal ions, despite their catalytic and biological importance. Most of the studies are confined to the halo-complexes of rhodium, palladium and platinum ions [11-13] and no heat data are available on their bonds with sulphur. The present investigation of the thermodynamics of the rhodium(III)-cysteine interaction is an attempt to fill this gap. This complex could also be isolated in the solid form and characterised on the basis of various physico-chemical techniques.

---

* Author for correspondence.

EXPERIMENTAL

Reagents and solutions

Rhodium(III) chloride was obtained from Johnson Mathey Ltd. (New Jersey). Cysteine hydrochloride, obtained from Koch-Light company (U.K.), was dried in vacuum over anhydrous $CaCl_2$ for 20 h at room temperature before use. All other chemicals were of AR (BDH) grade. The solutions were prepared in doubly distilled water. Carbon-dioxide free sodium hydroxide was used in pH-metric titrations.

Physical measurements

These were the same as reported earlier [14,15]. An expanded-scale pH-meter was standardised by the buffer solutions of 0.05 M potassium hydrogen phthalate (pH 4.01) and 0.05 M borax (pH 9.18) and checked by titrating 0.02 M perchloric acid with sodium hydroxide solution. The pH values measured and calculated from the analytical concentration of perchloric acid and activity coefficient of H^+ agreed within ± 0.004 pH units. Standardisation was checked both before and after each titration. The accuracy of the instrument was ± 0.02 pH units. The pH-metric titrations were carried out in a double-walled glass titration vessel provided with inlet and outlet tubes circulating water at a constant temperature (variation $\pm 0.1°C$) from a thermostat. After each addition of alkali titrant, the solution was stirred well with a magnetic stirrer and allowed to stand for the attainment of equilibrium. The following sets were prepared for titrations: (I) 5.0 ml $HClO_4$ (0.01 M); (II) 5.0 ml $HClO_4$ (0.01 M) + 5.0 ml cysteine (0.01 M), (III) 5.0 ml $HClO_4$ (0.01 M) + 5.0 ml cysteine (0.01 M) + 1.0 ml Rh(III) (0.01 M). The total volume in each case was made up to 25.0 ml with distilled water. The required ionic concentration was maintained with $NaClO_4$. Similar types of studies have also been carried out for the complexes of Rh(III) with α-alanine and 2-mercaptopropanoic acid.

Isolation of the complex

The solutions of Rh(III) chloride and cysteine hydrochloride were mixed in a 1 : 3 ratio and the pH of the mixture was raised to about 7.0 by adding an aqueous solution of sodium hydroxide. It was then concentrated by slow evaporation of the solvent on a water bath until yellow precipitates were formed which were filtered, washed several times with 50% alcohol and dried in a vacuum desiccator over silica gel. The complex was analysed chemically for metal, carbon, hydrogen and nitrogen. Found (%): Rh, 19.30; C, 20.42;

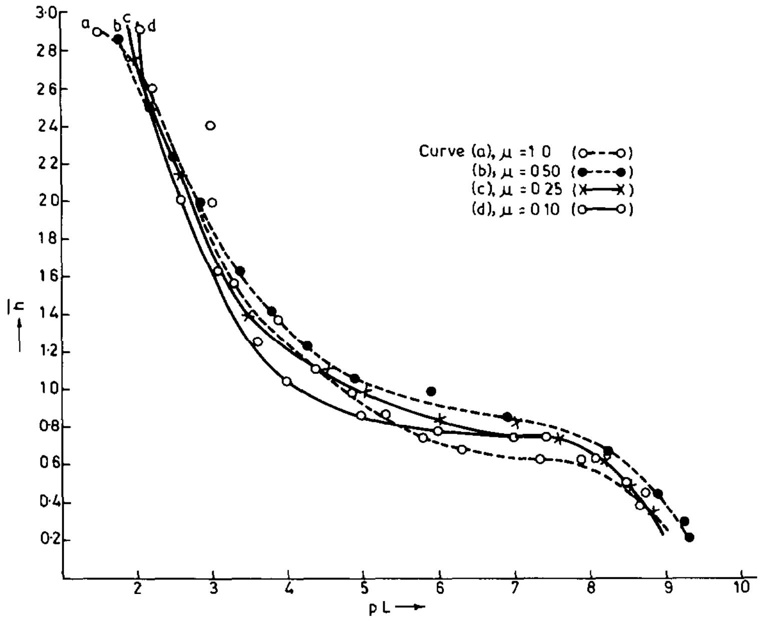


Fig. 1. Formation curve of Rh–cysteine complex at 25°C.

H, 2.76; N, 7.80; calc. for $Na_3[Rh(C_3H_5O_2NS)_3]$(%): Rh, 19.57; C, 20.50; H, 2.85; N, 7.94. The value of the magnetic moment at room temperature was found to be 0.72 thus indicating a diamagnetic character. The value of

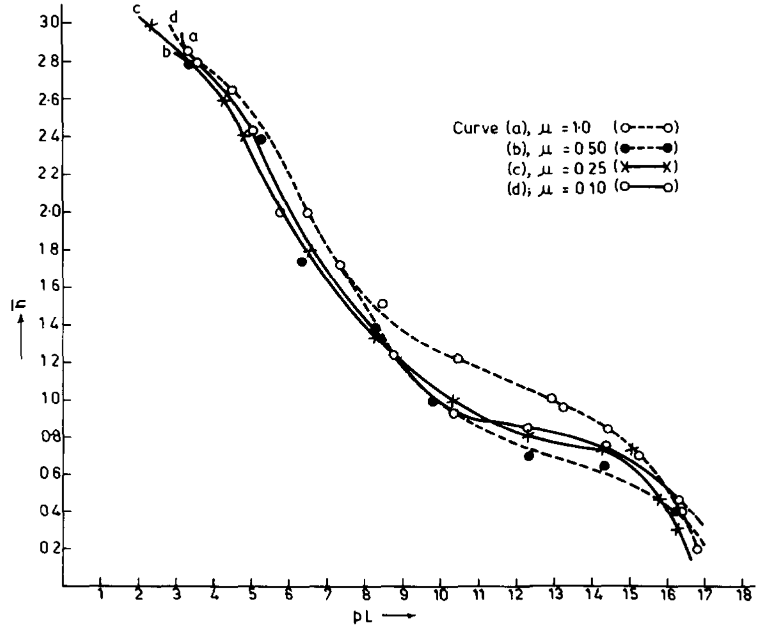


Fig. 2. Formation curve of Rh–α-alanine complex at 25°C.

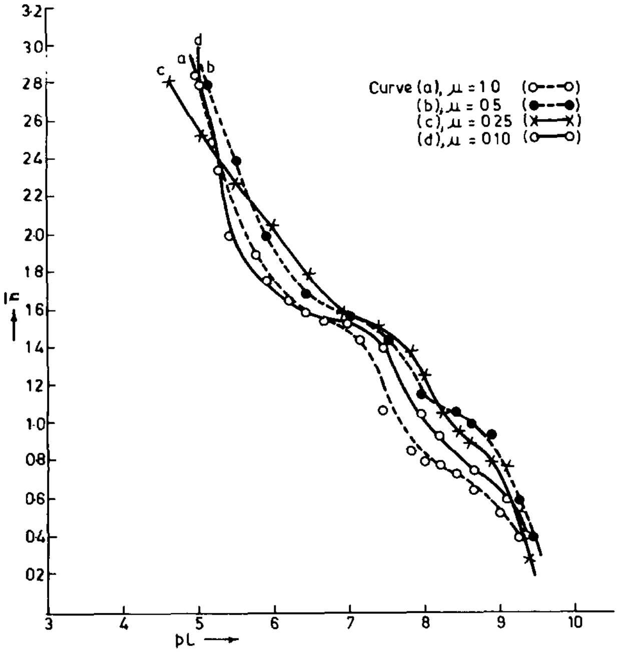


Fig. 3. Formation curve of Rh(III)-2-mercaptopropanoic acid complex at 25°C.

molar conductance (340.10 ohm^{-1} cm^2 mol^{-1}) indicated the presence of four ions.

Stability constants of the complexes

The stability constants of Rh(III) complexes of cysteine, α-alanine and 2-mercaptopropanoic acid were determined at three different temperatures, i.e., 25, 35 and 45°C, and at four different ionic concentrations, i.e., 1.0, 0.50, 0.25 and 0.10 M $NaClO_4$. Thus, an extrapolation to zero ionic strength was possible. The shapes of the formation curves ($\bar{n}$ vs. pL) for these ligands at 25°C are given in Figs. 1–3. Similar types of curves were obtained at 35 and 45°C. The equations used for the calculations were the same as those reported earlier [16,17].

The calculations were made on a DEC 2050 digital computer. The accuracy of pK values was 0.02 units and that of log K values was ± 0.04 log units. Therefore, the precision of ΔH and ΔS values was ± 0.56 cal mol^{-1} and ± 2.4 cal mol^{-1} deg^{-1}, respectively.

RESULTS AND DISCUSSION

Thermodynamic studies

The values of the dissociation constants for the ligands at three different temperatures and four ionic strengths (Table 1) have been found to be in

TABLE 1

pK values of ligands at different temperatures and ionic concentrations

Temp. (°C)	Molar conc. of $NaClO_4$	Cysteine			α-Alanine		2-Mercaptopropanoic acid	
		pK_1	pK_2	pK_3	pK_1	pK_2	pK_1	pK_2
25	1.00	1.96	8.67	10.35	9.56	10.40	3.70	9.55
	0.50	2.50	8.77	10.37	9.62	10.38	3.18	9.64
	0.25	2.53	8.84	10.40	9.66	10.42	3.24	9.71
	0.10	2.96	8.95	10.75	9.70	10.48	3.28	9.80
35	1.00	1.53	8.22	9.85	9.50	10.36	3.00	9.50
	0.50	1.98	8.25	9.85	9.58	10.39	3.10	9.64
	0.25	2.14	8.33	10.02	9.62	10.44	3.14	9.70
	0.10	2.35	8.35	10.06	9.66	10.48	3.20	9.80
45	1.00	1.53	8.10	9.72	9.00	9.64	2.94	9.35
	0.50	1.88	8.15	9.75	9.04	9.70	3.00	9.40
	0.25	1.98	8.25	9.95	9.10	9.78	3.12	9.50
	0.10	2.13	8.26	10.00	9.14	9.78	3.20	9.58

good agreement with values reported earlier [5,18]. A small difference may be due to the difference in temperature or ionic strength. Table 2 summarizes the values of formation constants and the values of ΔF, ΔH and ΔS are given in Table 3.

It was confirmed that, with the high ligand-to-metal ratio of 5 : 1 used in our studies, the presence of polynuclear species could be neglected since the formation curves determined from the ligand–metal ratios of 5 : 1 and 50 : 1 were found to be identical. The electronic spectra of these mixtures in the visible region further confirmed the presence of identical species in both

TABLE 2

Thermodynamic stability constants of Rh(III) complexes of cysteine, α-alanine and 2-mercaptopropanoic acid at three different temperatures

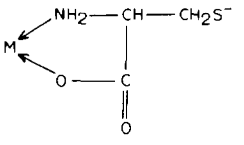
Ligands	Temp.	Log K_1	Log K_2	Log K_3	Log β_3
Cysteine	25	8.60	3.35	2.25	14.20
	35	8.25	3.20	2.15	13.60
	45	7.90	3.10	2.05	13.05
α-Alanine	25	15.95	8.00	4.35	28.30
	35	15.00	7.70	4.25	26.95
	45	13.85	7.45	4.05	25.23
2-Mercaptopropanoic acid	25	9.12	7.30	5.35	21.54
	35	8.85	7.12	5.12	21.09
	45	8.50	6.85	4.90	20.25

TABLE 3

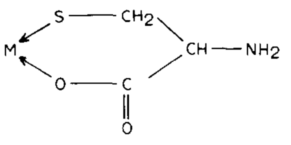
Stepwise ΔF,ΔH (kcal mol^{-1}) and ΔS (kcal mol^{-1} deg^{-1}) values for the formation of Rh(III) complexes with cysteine, α-alanine and 2-mercaptopropanoic acid at 25°C

Parameter	Cysteine complex	α-Alanine complex	2-Mercaptopropanoic acid complex
$-\Delta F_1$	11.73	21.67	12.40
$-\Delta F_2$	4.47	10.88	9.92
$-\Delta F_3$	3.07	5.91	7.27
$-\Delta H_1$	14.69	39.88	11.54
$-\Delta H_2$	4.30	12.59	7.55
$-\Delta H_3$	4.20	4.19	5.24
ΔS_1	-0.010	-0.061	$+0.003$
ΔS_2	-0.006	-0.006	$+0.008$
ΔS_3	-0.004	$+0.006$	$+0.007$

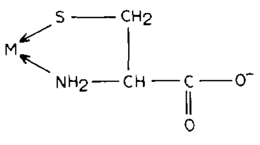
cases. The difference between the successive formation constants at 25°C is much larger for the bis-cysteinato complex (log $K_1/K_2 \approx 2.56$). This indicated the greater difficulty of formation of a 1 : 2 (M : L) complex compared to a 1 : 1 complex, which may be due to some steric reasons and statistical factors. Only two out of three donor groups in cysteine can bind to the metal ion simultaneously due to steric reasons [1] and, hence, a 1 : 1 metal–cysteine complex can have either of the following structures.



(I)



(II)



(III)

The fact that the value of log K_1 at 25°C for the Rh(III)–cysteine complex (log $K_1 = 8.6$) is almost equal to the formation of the Rh(III)–2-mercaptopropanoic acid chelate (log $K_1 \approx 9.0$) (Table 2), and very much different from the Rh(III)–α-alanine chelate (log $K_1 \approx 16.0$) shows that sulphydril and carboxyl are the donor groups which take part in the coordination.

The ΔH values reflect the changes in the number and strength of bonds made and broken during the process of coordination. The values of ΔH are, therefore, expected to throw some light on the type of bonding between the metal ion and the ligand molecules. These values for 1 : 3 (M : L) chelates of cysteine and 2-mercaptopropanoic acid were nearer to each other which, again, confirmed the coordination of cysteine through sulphydril and carboxyl groups (structure **II**).

Electronic spectrum of the complex

The electronic spectrum of the cysteine complex gave two spin-allowed bands at 19100 and 25500 cm^{-1} corresponding to the transitions $^1A_{2g} \rightarrow {}^1T_{1g}$ and $^1T_{2g}$, respectively, and a third spin-forbidden band involving a singlet → triplet transition was observed at 14410 cm^{-1} showing an octahedral structure of the complex. The values of $10Dq, B, \beta, C$ and LFSE (kcal mol^{-1}) calculated using descent in symmetry method, were found to be 21445, 400, 0.55, 2345 and 24.50, respectively.

IR studies

The coordination of cysteine through sulphydril and carboxyl groups was further confirmed from the IR spectrum of the complex. The spectrum of cysteine gave ν_{N-H} bands at 3000 and 3400 cm^{-1}, ν_{S-H} bands at 820 and 2450 cm^{-1} and ν_{COOH} bands at 650, 750, 1470 and 1590 cm^{-1}. ν_{S-H} bands completely disappeared and no change in ν_{N-H} bands was observed in the spectrum of the complex. ν_{COO^-} bands in the spectrum of the complex were observed at 1640 and 1420 cm^{-1}. It has been reported that the antisymmetric frequency ($\nu_{(as)COO^-}$) increases and the symmetric frequency ($\nu_{(s)COO^-}$) decreases and that the difference between the two is a measure of the M–OOC bonds [19]. The bands due to ν_{M-O} and ν_{M-S} were obtained at 420 and 350 cm^{-1}, respectively.

Thermal analysis

TG analysis of the complex indicated the absence of any type (crystal or coordinated) of water molecules.

REFERENCES

1 A.E. Martell and M. Calvin, Chemistry of Metal Chelate Compounds, Printice Hall, New York, 1952, p. 383.
2 H.B. Mathur, M.P. Gupta and C.B. Kavedia, Indian J. Chem., 4 (1966) 337.
3 R.G. Neville, J. Am. Chem. Soc., 79 (1957) 518.
4 R.G. Neville and G. Gorin, J. Am. Chem. Soc., 78 (1956) 4893.
5 S.K. Srivastava, E.V. Raju and H.B. Mathur, J. Inorg. Nucl. Chem., 35 (1973) 253.
6 C.L. Sharma and T.K. De, J. Less-Common Met., 70 (1980) 63.
7 G. Degischer and G.H. Nancollas, J. Chem. Soc. A, (1970) 1125.
8 V.S. Sharma and H.B. Mathur, Indian J. Chem., 3 (1965) 475.
9 E.V. Raju and H.B. Mathur, J. Inorg. Nucl. Chem., 30 (1968) 2181.
10 J.E. Letter, Jr. and J.E. Bauman, Jr., J. Am. Chem. Soc., 92 (1970) 437, 443.
11 H.L. Bott and A.J. Poe, J. Chem. Soc., (1965) 5931.
12 A.J. Poe, J. Chem. Soc., (1963) 183.

13 H.A. Droll, B.P. Block and W.C. Fernelius, J. Phys. Chem., 61 (1957) 1000.
14 I.P. Saraswat, C.L. Sharma and Anita Sharma, J. Indian Chem. Soc., 56 (1979) 928.
15 C.L. Sharma, T.K. De and P.K. Jain, Chem. Scr., 18 (1981) 79.
16 S.H. Simms, J. Am. Chem. Soc., 48 (1926) 1239.
17 H.M. Irwing and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
18 A.E. Martell and L.G. Sillen, Special Publication 17, The Chemical Society, London, 1964.
19 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd edn., Wiley-Interscience, New York, 1969, p. 232.