

## REACTIONS OF GALLOCYANINE METHYL ESTER WITH IONS OF NOBLE EARTHS\*

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Received March 22nd, 1978

Reactions of gallocyanine methyl ester with ten ions of noble earths have been followed spectrophotometrically in 10 to 30% (m/m) ethanol medium at pH 6.5 to 7.8. The trivalent cations and the ligand form complexes of  $ML_3$  type, their stability constants have been calculated by analysis of curves of concentration ratios and continuous variations.

Elements of the third group of the periodic system, especially lanthanoides, show low electronegativity<sup>1</sup> (Sc-Y-La 1.3-1.2-1.1). All the same, their affinity to oxygen is relatively marked, which is manifested by formation of usually labile complexes with organic oxygen ligands. For spectrophotometry the most advantageous are the ligands with O,O- and N,O-donor groups. Thus the used reagents are triphenylmethane dyestuffs, polyphenols, 8-hydroxyquinoline derivatives, *o*-hydroxyazo compounds *etc.* Out of these reagents gallocyanine was used for proof and photometric determination of a number of ions<sup>2</sup> involving also scandium in natural products<sup>3</sup>.

In analogy to gallocyanine, its methyl ester called prune reacts with many ions to give coloured solutions. This reagent gives more distinct reactions thanks to smaller number of ionized forms<sup>4</sup> and higher solubility especially in organic solvents. In mildly acidic to neutral media prune forms violet solutions with ions of the third group of the periodic system.

The aim of this work was to study the coordination equilibria of gallocyanine methyl ester with ions of noble earths in aqueous ethanolic medium and utilization of the reaction for photometric determination of these ions.

### EXPERIMENTAL

#### Solutions and Apparatus

The 0.01M stock solutions of salts of noble earths were prepared by dissolving the corresponding salt amount in water. Purity of the salts:  $ScCl_3 \cdot 6 H_2O$  95% (Lachema, Brno),  $YCl_3 \cdot 6 H_2O$  99% (Merck),  $La(NO_3)_3 \cdot 6 H_2O$  99% (Loba-Chemie, Wien),  $CeCl_3 \cdot 7 H_2O$  98.5% (Merck). The other

\* Part III in the series Complexes of Gallocyanine Methyl Ester with Inorganic Ions; Part II: This Journal 42, 241 (1977).

lanthanide salts were obtained on laboratory scale by dissolving the oxides  $\text{Pr}_6\text{O}_{11}$  (99.9% BDH, England),  $\text{Ho}_2\text{O}_3$  (spectroscopically pure),  $\text{Tb}_2\text{O}_3$  (99.9%),  $\text{Dy}_2\text{O}_3$  (97% — all the three Sojuzchimexport, USSR) in nitric acid;  $\text{Nd}_2\text{O}_3$  (99.9% BDH) and  $\text{Gd}_2\text{O}_3$  (pure, Sojuzchimexport) in hydrochloric acid; the obtained salts were recrystallized. Content of the noble earths in the stock solutions was determined by direct chelatometric titration with Xylenol Orange<sup>5</sup>. Titre of the used 0.01M chelator 3 was determined by titration with standard solution of lead(II) nitrate using Xylenol Orange<sup>6</sup>. Solutions of lower concentrations were prepared by corresponding dilution of the stock solutions with water.

The stock solution of  $2 \cdot 10^{-4}\text{M}$  galloycyanine methyl ester was prepared by dissolution of the weighed sample in 96% (m/m) ethanol. Preparation of the reagent and its purity check were described elsewhere<sup>7</sup>.

The colour reaction between the metal ions and the ligand takes place practically immediately in mildly acidic to neutral media. However, absorbance of the solutions is constant first 10 to 15 min after mixing of the components, hence the samples were measured always after 15 min. The absorbance of the complexes does not practically depend on ethanol concentration up to the content of 40% (m/m). Stability of the complexes was followed at three ethanol concentrations, its content of 10% (m/m) being the lowest possible for keeping the ligand in solution. Ionic strength has no influence on the absorbance of the complexes within the limits 1 0.025 to 0.25, hence all the measurements were carried out at the constant value 1 0.1 ( $\text{NaClO}_4$ ). With respect to presumed hydrolysis of some ions in slightly acidic medium the cations solutions were added to the measured solutions as the last component. In the buffers used pH was adjusted by mixing calculated amounts of 0.02M urotropine and 1M- $\text{HClO}_4$ .

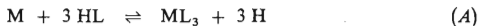
pH of the solutions was measured with PHM 4d and 26 pH-meters (Radiometer, Copenhagen) adjusted with aqueous potassium hydrogen phthalate. Determination of the pH-curves and, hence, region of formation of the complexes was carried out by titration with 0.01M-NaOH or HCl using an automatic burette ABU 12b connected with PHM 26 pH-meter and titrator TTT 11 (the whole apparatus Radiometer, Copenhagen). The absorbance was measured with recording apparatus Specord UV VIS (Zeiss, Jena) and Unicam SP 1800 (Pye, Cambridge) using 1 cm cells. The conditioned stability constants were calculated from both the concentration curves<sup>8</sup> and curves of continuous variations<sup>9</sup>.

## RESULTS AND DISCUSSION

Electronic configuration of elements of noble earths only causes slight changes in reactivities of the trivalent ions with inorganic and organic ligands. The complexes have high coordination numbers usually, but the metal-ligand bonds are predominantly ionic. This fact is confirmed also by the reactivity of the scandium subgroup and lanthanoids with galloycyanine methyl ester. In urotropine medium at  $\text{pH} > 6.5$  violet complexes are formed, colour of the solutions being identical with the ionic state  $\text{L}^-$  of the ligand. Absorption curves of the complexes at a constant ligand concentration and variable amount of the metal ion show a hypsochromic shift of the maximum by almost 135 nm ( $\lambda \approx 510$  nm) as compared with the maximum of the pure non-ionized ligand ( $\lambda_{\text{max}}$  644 nm), the result being the same in 10%, 20% and 30% (m/m) ethanol. In the whole studied pH region (pH 6.5 to 7.8) at the various ethanol concentrations the curves intersect (according to the kind of the ion) in isobestic points  $\lambda_{\text{iso}}$  548 to 554 nm and 702 nm (Fig. 1). In the wavelength ranges about

500 nm and 700 nm the complex absorbs more strongly than the ligand, therefore one coordination equilibrium is manifested by two isosbestic points. This single coordination equilibrium is unambiguously and concordantly confirmed by both curves of molar ratios and curves of continuous variations which give the composition of the complex with the component ratio  $M : L = 1 : 3$ .

In the pH region 6.5 to 7.8 the solution contains, besides predominant amount of the non-ionized ligand form HL, also the form  $L^-$  (its amount being about 0.5, 3, 8 and 13% at pH 6.5, 7.0, 7.5 and 7.8, respectively). Thus the coordination equilibrium can be formulated as Eq. (A) for pH 6.5 to 7.5, whereas at higher pH Eq. (B) also must be taken into account (ionic charges are omitted in all the equations for simplicity).



The equilibria are characterized by the following constants:

$$*\beta_{13} = [ML_3][H]^3/[M][HL]^3 \quad (1)$$

$$\beta_{13} = [ML_3]/[M][L]^3, \quad (2)$$

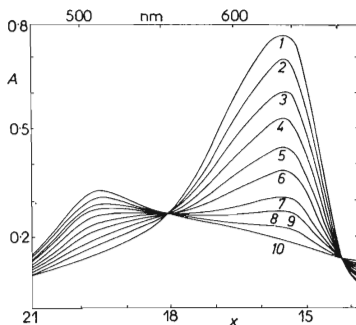


FIG. 1

Absorption Curves of Solution of "Prune" and  $Tb^{3+}$  Ions

$c_L = 2 \cdot 10^{-5} \text{ mol}^{-1}$ , 20% (m/m) ethanol, pH 7.16,  $d$  1 cm,  $I_{0.1}$ ,  $c_{Tb}$ : 1.0,  $2.1 \cdot 10^{-6}$ ,  $3.2 \cdot 10^{-6}$ ,  $4.3 \cdot 10^{-6}$ ,  $5.4 \cdot 10^{-6}$ ,  $6.5 \cdot 10^{-6}$ ,  $7.6 \cdot 10^{-6}$ ,  $8.7 \cdot 10^{-6}$ ,  $9.1 \cdot 10^{-5}$ ,  $10.2 \cdot 10^{-5} \text{ mol}^{-1}$ ,  $\bar{\nu} \cdot 10^{-3}, \text{ cm}^{-1}$ .

out of which (2) represents the stability constant, too. If  $K_{a2}$  is the constant of the equilibrium  $\text{HL} \rightleftharpoons \text{H}^+ + \text{L}^-$ , then

$$*\beta_{13} = \beta_{13} \cdot K_{a2}^3 \quad (3)$$

The conditioned constant  $\beta'_{13}$  will be defined by Eq. (4)

$$\beta'_{13} = [\text{ML}_3]/[\text{M}][\text{L}']^3 = [\text{ML}_3]/[\text{M}]([\text{L}] \cdot \alpha_{\text{L(H)}})^3, \quad (4)$$

where  $[\text{L}'] = [\text{HL}] + [\text{L}^-]$  and  $\alpha_{\text{L(H)}} = 1 + K_{a2}^{-1} \cdot [\text{H}]$ . For high pH values it is  $\beta'_{13} \approx \beta_{13}$ . In the region  $\text{pH} < 7.5$  where the predominant part of the quantitative measurements were carried out the reaction will fit the simple formalism in which  $[\text{L}'] \equiv [\text{HL}]$ ; it is

$$*\beta = \beta'_{13} \cdot [\text{H}]^3 \quad (5)$$

For calculation of the conditioned stability constants  $\beta'_{13}$  from the curves of continuous variations the method by Klausen<sup>9</sup> was used. For the complex  $\text{ML}_3$  it is

$$[\text{M}] = c(1 - x) - [\text{ML}_3] \quad (6)$$

and

$$[\text{L}'] = cx - 3[\text{ML}_3], \quad (7)$$

where  $c = c_{\text{M}} + c_{\text{L}}$  and  $x = c_{\text{L}}/c$ .

From Eqs (4), (6) and (7) and by modification the general equation of the Job's curve for the complex 1 : 3 is obtained:

$$(1 - x - y)(x - 3y)^3 - (1/\beta'_{13}c^3)y = 0, \quad (8)$$

where  $y = [\text{ML}_3]/c$ .

The parameter  $1/\beta'_{13}c^3$  gives the deviation of the real Job's curve of the complex from the curve of the complex quantitatively formed. From the published<sup>9</sup> values of the dependence  $y = f\{\log(\beta'_{13}c^3)\}$  provided by computer it is possible to construct a graph for  $x = 0.75$ ; this graph and the experimental values  $y = 0.25$  ( $A_{\text{max}}/A_{0,\text{max}}$ ) obtained from the maxima of theoretical and real Job's curves make it possible to determine the conditioned stability constant  $\beta'_{13}$ .

For verification of the used calculation method of the conditioned stability constants curves were constructed<sup>2</sup> as a function  $y = f(x)$ . The Job's function  $|Y|$  is proportional to concentration of the complex in solution and, hence, it represents a function of  $y$ , too:

$$|Y| = \varepsilon \cdot d \cdot c \cdot y \quad (9)$$

For the quantitatively formed complex the  $y$  function will be equal to the limit value 0.25, so that

$$|Y_0| = \varepsilon \cdot d \cdot c \cdot 0.25. \quad (10)$$

Introduction of  $\varepsilon$  value in Eq. (9) enables to calculate and represent graphically the curves as functions  $y = f(x)$ . The tangent constructed from the right-side end point ( $x = 1$ ) must reach the value  $y = 0.25$  for  $x = 0.75$ . In this case it is parallel to the tangent calculated and constructed according to the general equation<sup>10</sup> (for the complex  $M_mL_n$ )

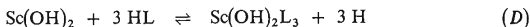
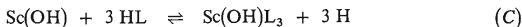
$$y = -(1/m)x + (n-1)/(m(m+n-1)) \quad \text{for } n \geq 2 \quad (11)$$

which, in the particular case of the complex  $ML_3$ , gives the expression  $y = -x + 0.667$ . In this way the complex  $ML_3$  was proved to be the only one in the solution, and the used method of calculation of the conditioned stability constants  $\beta'_{13}$  from the curves of continuous variations proved to be suitable.

Correctness of the conditioned stability constant values  $\beta'_{13}$  was verified by calculation of the constants from the curves of concentration ratios by the method of Klejner<sup>8</sup>. Results of the both methods showed a very good agreement.

From graphical dependence of the conditioned constants  $\log \beta'_{13}$  on pH for lanthanoides it follows that the reaction involves splitting off of three protons, which confirms the simple coordination equilibrium (A). Therefore, from Eqs (5) and (3) the stability constants  $*\beta_{13}$  and  $\beta_{13}$  could be calculated (they are given in Table I along with the molar absorption coefficients).

In the case of scandium and yttrium complexes slope of the dependence  $\log \beta'_{13} = f(\text{pH})$  has a substantially lower value ( $\varrho = 1.6$  for Sc,  $\varrho = 1.8$  to 2.0 for Y). Thus in the both cases influence of hydrolysis of the ions can be expected during formation of the complexes. Hydrolysis of the ions  $\text{Sc}^{3+}$  generates the hydroxido complexes<sup>12</sup>  $\text{ScOH}^+$ ,  $\text{Sc}(\text{OH})_2^+$ ,  $\text{Sc}_2(\text{OH})_2^{4+}$ , higher polynuclear complexes<sup>13</sup> being possible, too. However, the hydroxido complexes can react with the ligand either in direct reaction



or *via* substitution of hydroxyl group by the ligand

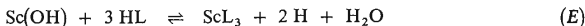


TABLE I  
Stability Constants  $\beta_{13}$  and  $\beta_{13}$  of Complexes of "Prune" with Lanthanoides (1.0:1 NaClO<sub>4</sub>)

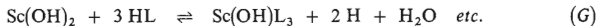
Ion	10% (m/m) ethanol			20% (m/m) ethanol			30% (m/m) ethanol		
	$\log \beta_{13}^a$	$\log \beta_{13}^b$	$\epsilon \cdot 10^{-4}$ (pH)	$\log \beta_{13}^a$	$\log \beta_{13}^b$	$\epsilon \cdot 10^{-4}$ (pH)	$\log \beta_{13}^a$	$\log \beta_{13}^b$	$\epsilon \cdot 10^{-4}$ (pH)
La <sup>3+</sup>	-4.42	19.55	6.43 (7.23)	-4.78	19.51	7.91 (7.40)	-5.81	18.85	6.28 (7.22)
Ce <sup>3+</sup>	-4.89	19.08	6.24 (7.57)	-4.69	19.61	7.60 (7.04)	-4.54	20.12	5.46 (6.86)
Pr <sup>3+</sup>	-4.63	19.34	4.86 (7.22)	-4.93	19.37	3.02 (7.51)	-4.81	19.85	3.28 (7.13)
Nd <sup>3+</sup>	-5.40	18.54	2.88 (7.24)	-5.58	18.72	2.90 (7.48)	-6.07	18.59	1.40 (7.71)
Gd <sup>3+</sup>	-4.38	19.59	3.61 (7.21)	-4.52	19.78	2.80 (7.11)	-4.68	19.98	2.66 (7.41)
Tb <sup>3+</sup>	-4.43	19.54	7.06 (7.45)	-4.52	19.78	8.20 (7.11)	-5.21	19.45	7.32 (7.02)
Dy <sup>3+</sup>	-4.40	19.57	7.10 (7.21)	-4.91	19.39	6.82 (7.50)	-4.84	19.82	7.03 (6.83)
Ho <sup>3+</sup>	-4.54	19.43	6.04 (7.45)	-4.97	19.33	7.84 (7.11)	-4.64	20.02	6.98 (7.22)

<sup>a</sup>  $\beta_{13}$  =  $\beta_{13} \cdot [H]^3$  (the values  $\beta_{13}$  are average values obtained for 5 wavelengths), <sup>b</sup>  $\beta_{13}$  =  $\beta_{13}/K_{s2}$  for 6.5 < pH < 7.8. The used values pK<sub>s2</sub> are 7.99, 8.10 and 8.22 for 10%, 20% and 30% ethanol, respectively (see ref.<sup>11</sup>). <sup>c</sup> For 650 nm  $\epsilon$  = 3 $\epsilon_L$  -  $\epsilon_{comp}$ .

TABLE II  
The Conditioned Stability Constants  $\beta''_{13}$  of Complexes of "Prune" with Scandium and Yttrium (1:0:1 NaClO<sub>4</sub>)

Complex	10% (m/m) ethanol			20% (m/m) ethanol			30% (m/m) ethanol		
	pH	$\log \beta''_{13}$	$\epsilon_{650} \cdot 10^{-4}$	pH	$\log \beta''_{13}$	$\epsilon_{650} \cdot 10^{-4}$	pH	$\log \beta''_{13}$	$\epsilon_{650} \cdot 10^{-4}$
ScL <sub>3</sub>	7.06	16.65	—	6.95	16.62	—	6.91	16.82	4.61
	7.27	17.31	—	7.11	16.89	7.40	7.20	17.09	—
	7.55	17.49	6.65	7.49	17.22	—	—	—	—
YL <sub>3</sub>	6.80	16.55	—	6.78	17.09	—	6.86	17.13	—
	6.91	16.92	—	6.96	17.35	—	7.50	17.56	3.99
	7.73	17.79	3.79	7.62	17.59	4.01	—	—	—

The values  $\beta''_{13}$  are average values of determinations at 5 wavelengths.  $\epsilon = 3\epsilon_L - \epsilon_{\text{compl}}$ .



The the conditioned constant  $\beta''_{13}$  will be defined as follows

$$\begin{aligned} \beta''_{13} &= [\text{ScL}'_3]/[\text{Sc}'][\text{L}']^3 = \\ &= [\text{ScL}_3] \cdot \alpha_{\text{ScL}_3}/[\text{Sc}] \cdot \alpha_{\text{Sc}(\text{OH})}([\text{L}] \cdot \alpha_{\text{L}(\text{H})})^3. \end{aligned} \quad (12)$$

Analogous situation is encountered with yttrium, though the stability constants of the hydroxido complexes are not as high as those of scandium<sup>12,13</sup>. That is why it was impossible to determine the values  $^*\beta_{13}$  and  $\beta_{13}$  for complexes of "prune" with the two ions. Values of the conditioned constants  $\beta''_{13}$  are given in Table II for several pH values.

At pH 6.5 to 7.5 stability of the complexes of noble earths with "prune" is sufficient for utilization of the dyestuff for spectrophotometric determination of the noble earths. For the determination a slight excess of the reagent is sufficient, and 15 min after mixing the components it must be waited for the colouration of the solution to be fixed. When using  $2 \cdot 10^{-5} \text{M}$  reagent, 10% (m/m) ethanol and  $\text{pH} \approx 7$  the following reliable determinations are possible: 0.04 to 0.292  $\mu\text{g}$  Sc/ml (standard deviation  $s = 0.0185$  for 0.10  $\mu\text{g}$  of the metal in 1 ml of solution), 0.09 to 0.603  $\mu\text{g}$  Y/ml ( $s = 0.0155$  for 0.45  $\mu\text{g}$  Y/ml), 0.13 to 0.94  $\mu\text{g}$  La/ml ( $s = 0.0086$  for 0.52  $\mu\text{g}$  La/ml), 0.14 to 0.95  $\mu\text{g}$  Ce/ml ( $s = 0.0086$  for 0.56  $\mu\text{g}$  Ce/ml), 0.14 to 0.94  $\mu\text{g}$  Pr/ml ( $s = 0.0129$  for 0.56  $\mu\text{g}$  Pr/ml), 0.144 to 0.95  $\mu\text{g}$  Nd/ml ( $s = 0.0103$  for 0.57  $\mu\text{g}$  Nd/ml), 0.157 to 1.05  $\mu\text{g}$  Gd/ml ( $s = 0.0138$  for 0.63  $\mu\text{g}$  Gd/ml), 0.16 to 1.05  $\mu\text{g}$  Tb/ml ( $s = 0.0142$  for 0.64  $\mu\text{g}$  Tb/ml), 0.16 to 1.08  $\mu\text{g}$  Dy/ml ( $s = 0.0125$  for 0.65  $\mu\text{g}$  Dy/ml), 0.16 to 1.10  $\mu\text{g}$  Ho/ml ( $s = 0.0129$  for 0.66  $\mu\text{g}$  Ho/ml). The standard deviation  $s$  was calculated from five parallel analyses at  $\lambda$  510 nm.

The dyestuff was also tried as indicator for chelatometry of noble earths. It is not recommended to use the reagent as metallochromic indicator for determination of the mentioned metals, because the colour change is little marked.

*The authors are indebted to Dr R. Pastorek, Inorganic and Physical Chemistry Department, Palacký University, Olomouc, for kindly supplying some salts of noble earths.*

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Translated by J. Panchartek.