

## Spectrophotometric Study of Co(II) – Chrome Azurol S Chelate

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With 5 Figures

### Summary

The formation of a red coloured chelate between divalent cobalt and tri sodium salt of sulpho-dichlorohydroxy dimethyl fuchson dicarboxylic acid (CAS) with  $\lambda_{\max}$  at 450 m $\mu$  has been reported. The composition of the chelate employing spectrophotometric method has been determined by the continuous variation, mole ratio and slope ratio methods. The chelate has a composition corresponding to Co(CAS)<sub>2</sub> and is stable between the pH range 10.5 to 11.5. Stability constant of the chelate has been found to be (log K = 8.00) involving a free energy change of formation  $\Delta G^\circ = -11.0$  K cal.

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Chrome Azurol S (colour Index No. 43825, 3''-sulpho-2'':6'' di chloro-3:3'-dimethyl-4-hydroxyfuchson-5:5' dicarboxylic acid, abbreviated CAS) is an important member of the hydroxy tri phenyl methane group of dyes and has often been employed in spectrophotometric analysis.

CAS has been used for the determination of copper (II)<sup>1)</sup> in acid and ammonical solutions and for the determination of fluoride with beryllium<sup>2)</sup> and aluminium<sup>3)</sup> lakes. DEY and coworkers<sup>4)</sup> have demonstrated the use of CAS in the complexometric determination of palladium and thorium and in a recent communication, MUSHRAN and coworkers<sup>5)</sup> have described the determination of micro amounts of quadrivalent vanadium with the reagent. In this communication are presented the results on the composition and stability of a new chelate of cobalt (II) with chrome Azurol S.

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1) M. THEIS, Z. analyt. Chem. **144**, 275 (1955).

2) L. SILVERMAN and M. E. SHIDELER, Annal. Chem. **31**, 152 (1959).

3) B. J. MACNULLY and L. D. WOOLARD, Annal. Chim. Acta **14**, 452 (1956).

4) S. C. SRIVASTAVA, S. N. SINHA and A. K. DEY, Bull. chem. Soc. (Japan) **3b**, 268 (1963).

5) P. SANYAL and S. P. MUSHRAN, Mikro. Chim. Acta **5-6**, 959 (1965).

## Experimental

**Apparatus and Reagents:** Spectrophotometric measurements were made with a Unicam SP 500 spectrophotometer and 1.00 cm glass cells, pH measurements were made with a direct reading Leeds and Northrup pH meter with glass and calomel electrodes.

An (A.R. B.D.H.) sample of cobaltous sulphate was used and solutions of necessary concentration were prepared in double distilled water and was standardised by  $\alpha$ -nitroso- $\beta$ -naphthol B.D.H. indicator. Fresh solutions of chrome Azurol S were prepared in double distilled water by weighing.

For adjustment of pH, A.R. B.D.H. ammonia solution was employed.

## Results

**Colour of the chelate:** Instantaneous colour formation takes place when reagent and metal solution are mixed at pH 11.0 at room temperature. The chelate was found to be very stable and no effect on the stability of the chelate was observed when the order of mixing of reagents was altered.

**Nature of Chrome Azurol S with change in pH:** A detailed study of the visible spectra (350–700  $m\mu$ ) of pure chrome Azurol S over the pH range (1.4–12.5) was made. The wavelength of maximum absorbance of the reagent between pH 1.5–5.0 is 460 and 490  $m\mu$ , whereas between pH 5.4–11.5 it shifts to 430  $m\mu$  and above 11.4 is 600  $m\mu$ .

**Nature and stoichiometry of the chelate:** The nature of the chelate was determined by the method of VOSBURGH and COOPER<sup>6)</sup> at

Curve	Final concentration $M \cdot 10^{-5}$		Ratio Co(II):CAS
	CoSO <sub>4</sub>	CAS	
A	0.00	4.0	0 : 1.0
B	8.00	4.0	1 : 0.5
C	4.00	4.0	1 : 1.0
D	2.00	4.0	1 : 2.0
E	1.33	4.0	1 : 3.0

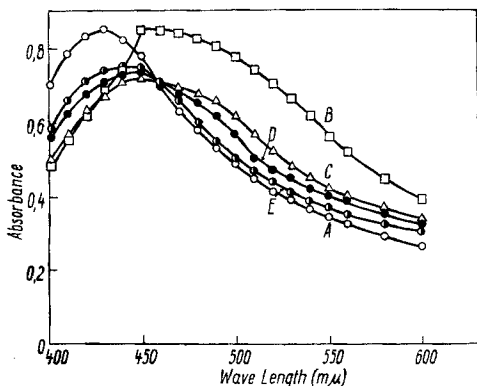


Fig. 1. Absorption spectra of Co(II)–CAS chelate Nature of the complex formed; total volume 50 ml, pH = 11.0, Temp. = 25°C

<sup>6)</sup> W. C. VOSBURGH and G. R. COOPER, J. Amer. chem. Soc. **63**, 437 (1941); **4**, 1630 (1942).

pH 11.0. The results are represented graphically in Fig. 1, from which it is clear that the  $\lambda_{\max}$  of the reagent is at 430 m $\mu$  but for the chelate it shifts to 450 m $\mu$  and there is a clear indication of the formation of only one complex in the system under the conditions used.

JOB's method of continuous variation showed the formation of a 1:2 chelate [cobalt (II) : CAS] at 520 m $\mu$  and pH 11.0 when the concentration of the interacting solutions were the same (Fig. 2a). The results shown in the Fig. 2b were obtained when the concentration ratios of chrome Azurol S to cobalt sulphate were 0.5 (curve A) and 2.0 (curve B).

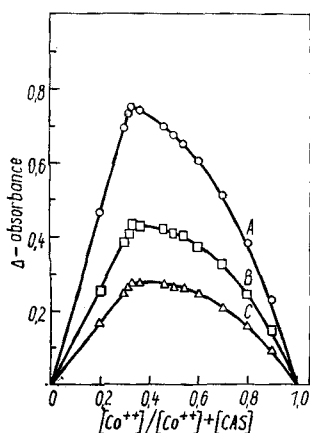


Fig. 2a. Determination of the composition of the chelate by JOB's method of continuous variation at 520 m $\mu$ ; pH = 11.0, curve A,  $3.33 \cdot 10^{-4}$  M; curve B,  $2.00 \cdot 10^{-4}$  M; curve C,  $1.33 \cdot 10^{-4}$  M

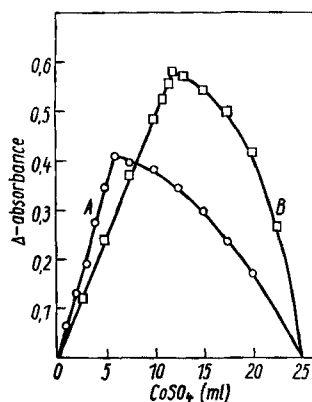


Fig. 2b. Determination of the composition of the chelate by JOB's method of continuous variation at 520 m $\mu$ ; pH = 11.0; curve A,  $1.00 \cdot 10^{-4}$  M, CAS; curve B,  $2.00 \cdot 10^{-4}$  M, CAS

Results obtained from the continuous variation method were corroborated by the mole ratio (Fig. 3) and slope ratio (Fig. 4) methods.

The pH stability range of the chelate was obtained by measuring the absorbance of mixtures containing cobalt sulphate and CAS in a 1:2 ratio at different pH and varying wavelengths. The chelate was found to be stable in the pH range 10.5—11.5.

7) P. JOB, *Compt. Rend.* **180**, 928 (1925). *Ann. Chim. (Paris)* **10**, 9, 113 (1928).

8) J. H. YOE and A. L. JONES, *Ind. Engng. Chem. Analyt. Ed.* **16**, 111 (1944).

9) A. E. HARVEY and D. L. MANNING, *J. Amer. chem. Soc.* **17**, 4488 (1950); **74**, 4744 (1952).

Evaluation of Stability Constant: For two concentrations ( $a_1, b_1$ ) and ( $a_2, b_2$ ) of the reactants having the same absorbance i.e. for the same value of the concentration of the complex  $x$ , for a chelate of the type 1:2, the equilibrium constant is given by:

$$K = \frac{x}{(a_1 - x)(b_1 - 2x)^2} = \frac{x}{(a_2 - x)(b_2 - 2x)^2}$$

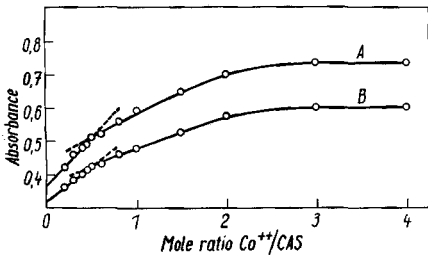


Fig. 3. Determination of the composition by the mole ratio method at 520 m $\mu$ ; pH = 11.0; Final conc. of CAS, curve A,  $10.00 \cdot 10^{-5}$  M, curve B,  $8.00 \cdot 10^{-5}$  M

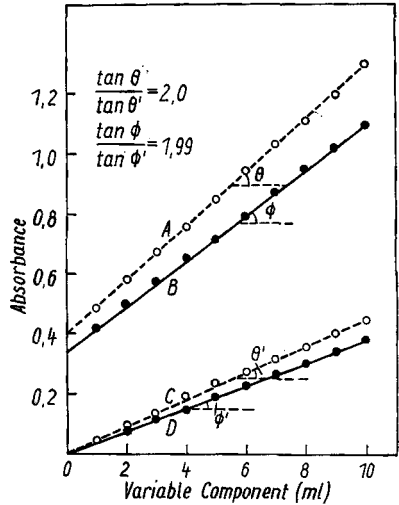


Fig. 4. Determination of the composition by the slope ratio method, curve A, 520 m $\mu$ ; curve B, 530 m $\mu$  (CoSO<sub>4</sub> varying); curve C, 520 m $\mu$ ; curve D, 530 m $\mu$  (CAS varying). 10 ml excess component of  $5.00 \cdot 10^{-4}$  M, x ml of variable component ( $1.66 \cdot 10^{-4}$  M) + (15 - x) ml of water

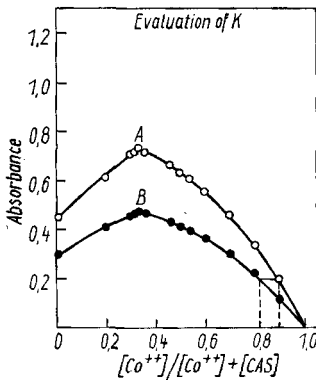


Fig. 5. Determination of stability constant by DEY and coworker's method. Curve A, CoSO<sub>4</sub> and CAS,  $2.00 \cdot 10^{-4}$  M; curve B, CoSO<sub>4</sub> and CAS,  $1.33 \cdot 10^{-4}$  M

This gives a quadratic equation in  $x$  which can be easily solved and the value of the  $x$  is obtained.

For two mixtures having the same optical density i.e. 0.2 (Fig. 5) the value of  $x$  was found to be  $0.0326 \cdot 10^{-4}$  M and the stability constant was evaluated to be  $\log K = 8.00$ , using the equation:

$$K = \frac{x}{(a - x)(b - 2x)^2}$$

From the value of  $\log K$  and making use of the relation  $\Delta G^\circ = -RT \log K$ , the free energy change during the formation of the chelate was estimated as  $-11.0$  K cal.

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