

## **Physico Chemical Studies on the Metal Chelates of Nitroso R Salt, Thoron, Chromotrope 2 B and Chrome Azurol S in Aqueous Solution**

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### **Abstract**

Composition and stability of palladium-Nitroso R Salt chelate, lanthanum, thorium, uranium and palladium chelates of Thoron, lanthanum-Chromotrope 2 B chelate and palladium-Chrome Azurol S chelate have been reported. The range of stability of the chelates with pH have also been determined. The use of Chrome Azurol S, Chromotrope 2 B, Murexide, Thoron, Quinizarin sulphonic acid, and gallocyanine in the complexometric determination of thorium against EDTA has also been reported.

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The foundation of coordination chemistry was laid nearly seventy years ago and during these years remarkable progress has been made in this branch of chemical science and numerous new compounds of this class have been investigated. The study of coordination chemistry has enlarged in scope and now includes not only the chemistry of inorganic compounds but large portions of organic and biochemistry as well. A large number of organic compounds have the property of coordinating with metal ions and many of these produce coloured compounds. The study of these coloured complexes has led to their manifold applications in the realm of analytical chemistry, particularly to colorimetric methods of analysis and in complexometric titration methods. The study of coloured complexes received a great impetus by the introduction of sensitive spectrophotometers nearly four decades ago. The present work deals with the formation of a number of coloured metal chelates in solution, with some chromogenic organic compounds capable of coordinating with metal ions. Metal chelates of the following reagents have been investigated and the results are presented in the preceding pages.

- (I)  $\alpha$ -nitroso  $\beta$ -naphthol-3 : 6-disulphonic acid (Nitroso-R-Salt).
- (II) 1-(*o*-arsonophenylazo)-2-naphthol 3 : 6 disulphonic acid (Thoron).
- (III) *p*-nitrobenzene azochromotropic acid (Chromotrope 2-B).
- (IV) Sulphodichloro-hydroxy dimethyl fuchson dicarboxylic acid (Chrome Azurol S).

When a metal ion combines with a ligand having only one point of attachment, i.e., one pair of electrons, the product is a metal complex. If, however, the coordinating ligand has more than one donor group, a metal chelate is formed. Thus chelates possess a ring structure and have characteristics specific to themselves, which make them a distinct class among complex compounds.

Metal chelates have found various applications in chemical and biological fields. One of the important applications of organic chelating agents is in the colorimetric determination of metals and an enormous amount of work has been done in this direction.

In spite of the extensive study of the chromogenic properties of organic chelating agents, much of the work has been directed to the working out of the details of the colorimetric methods on an empirical basis, and the study of the composition and characteristics of metal chelates in such reactions has not received proper attention. It must be emphasised that it is necessary to direct studies towards this aspect, in order to obtain fuller information on the nature and properties of the metal chelates in these chromogenic reactions. Various experimental methods for the spectrophotometric investigations of coloured compounds have been described. The common methods employed are (I) the method of continuous variations<sup>1)</sup>, (II) slope ratio method<sup>2)</sup>, and (III) mole ratio method<sup>3)</sup>. Several other methods have also been suggested, associated with the names of BENT and FRENCH<sup>4)</sup>, EDMONDS and BIRNBAUM<sup>5)</sup>, MOLLAND<sup>6)</sup>, BJERRUM<sup>7)</sup>, NEWMAN and HUME<sup>8)</sup>, JENSEN<sup>9)</sup>, YATSIMIRSKII<sup>10)</sup>, etc. In the present work only the first three methods have been employed which, besides being popular, are convenient and yield satisfactory results.

Several methods are available for the evaluation of stability constants from absorbance data. In recent years DEY and coworkers<sup>11)</sup> have worked

<sup>1)</sup> P. JOB, *Compt. rend.* **180**, 928 (1925); *Ann. Chim. (X)* **9**, 113 (1928).

<sup>2)</sup> J. H. YOE and A. L. JONES, *Ind. Eng. Chem., Analyt. Ed.* **16**, 111 (1944).

<sup>3)</sup> A. E. HARVEY and D. L. MANNING, *J. Amer. chem. Soc.* **72**, 4488 (1950); **74**, 4744 (1952).

<sup>4)</sup> H. E. BENT and C. L. FRENCH, *J. Amer. chem. Soc.* **63**, 568 (1941).

<sup>5)</sup> S. M. EDMONDS and N. BIRNBAUM, *J. Amer. chem. Soc.* **63**, 1471 (1941).

<sup>6)</sup> J. MOLLAND, *J. Amer. chem. Soc.* **62**, 54 (1940).

<sup>7)</sup> J. BJERRUM, *Metal Ammine Formation in Aqueous solution*, P. Haase, Copenhagen (1941).

<sup>8)</sup> L. NEWMAN and D. N. HUME, *J. Amer. chem. Soc.* **79**, 4571 (1957).

<sup>9)</sup> M. J. JENSEN, *Rec. Trav. Chim.* **75**, 1397 (1956).

<sup>10)</sup> K. B. YATSIMIRSKII, *Zhur. neorg. Khim. (I)* **10**, 2306 (1956).

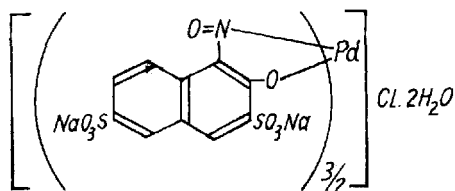
<sup>11)</sup> A. K. MUKHERJI and A. K. DEY, *J. Inorg. Nucl. Chem.* **6**, 314 (1958); *Analyt. Chim. Acta* **18**, 324 (1958).

out a method based on the comparison of the compositions of systems having an identity of colour, i.e., the same absorbance values. Their method is similar to the procedure described by ANDERSON et al., but has the advantage that it can be applied to systems where one of the interactants is coloured. In the method of ANDERSON<sup>12)</sup>, however, the prerequisite condition is that both the metal ion and the chelating agents must be colourless. Thus the method of DEY et al. can be applied to systems involving coloured ligands, as in the present work, and has, therefore, wider applications.

In the present work, the stabilities of the systems investigated have been determined by the method of DEY et al., and the values of the stability constants have been compared with those obtained by the mole ratio method of YOE and JONES, through a calculation of the degree of dissociation. A fair agreement is observed between the values obtained by the two methods. It is, however, felt that the former method is more convenient and may probably be regarded as more reliable.

#### Pd-Nitroso R Salt Chelate

The formation of a brownish red coloured chelate between  $\alpha$ -nitroso  $\beta$ -naphthol-3:6-disulphonic acid (Nitroso-R-Salt; abbreviated as NRS) and bivalent palladium has been reported here for the first time. The chelate has a composition involving three moles of the reagent and two atoms of palladium, having a  $\lambda_{\max}$  at 420 m $\mu$ . The chelate is stable between a wide range of pH, i.e., between 1.0 and 11.0. It has been suggested that palladium is chelated between the phenolic oxygen and the nitrogen of the nitroso group, as follows:



#### Metal chelates of thoron

A detailed study has been made of the metal chelates of lanthanum (III), thorium (IV), uranyl (II) and palladium (II) with 1-(*o*-arsonophenyl azo)-2-naphthol 3:6 disulphonic acid. The disodium salt is well known as a colori-

<sup>12)</sup> R. C. ANDERSON and R. T. FOLEY, J. Amer. chem. Soc. **70**, 1195 (1948); **71**, 909 (1949).

metric reagent for thorium and has hence been assigned such trivial names as Thoron, Thorin, Thorone, and Thoronol. It is also available commercially under the trade names of Naphthazarine, Naphtharson and APANS. Detailed studies, however, on the compositions of metal chelates of Thoron are not on record, except in case of thorium<sup>13)</sup>, for which too, divergent results have been reported. In the present study it has been noted that the reagent possesses the characteristics of a colloidal electrolyte<sup>14)</sup> and it has been recommended that physico-chemical measurements should be performed with extremely dilute solutions. The results on the characteristics and the composition of the different metal chelates of Thoron studied here are summarised in the following table.

Table 1  
Composition of the Thoron Chelates

Chelate	$\lambda_{\max}$ m $\mu$	Composition M:Ke	pH range of stability
La (III)-Thoron	515	1:2	4.0— 8.0
Th (IV)-Thoron	515	1:2	1.0— 6.5
UO <sub>2</sub> (II)-Thoron	510	1:1	2.5— 5.0
Pd (II)-Thoron	525	1:1	1.0—12.5

It was also ascertained that under the conditions of study only one chelate is formed in each of the systems investigated.

Table 2  
Stability of the Thoron Chelates

Chelate	pH	log K	$\Delta F^\circ$ at 25°C (K Cals)
LaCl <sub>3</sub> -Thoron	5.5	9.92 ± 0.25	-13.7 ± 0.3 (a)
		10.25 ± 0.20	-14.4 ± 0.3 (b)
ThCl <sub>4</sub> -Thoron	3.0	9.40 ± 0.30	-13.0 ± 0.4 (a)
		9.80 ± 0.20	-13.6 ± 0.3 (b)
UO <sub>2</sub> SO <sub>4</sub> -Thoron	3.0	4.25 ± 0.29	- 5.9 ± 0.3 (a)
		4.54 ± 0.15	- 6.3 ± 0.2 (b)
PdCl <sub>2</sub> -Thoron	3.0	4.38 ± 0.15	- 6.1 ± 0.2 (a)

(a) Method of DEY et al.

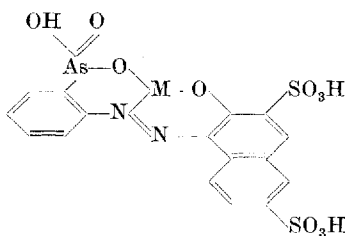
(b) Mole ratio method

<sup>13)</sup> M. B. JOHNSTON, A. J. BARNARD JR. and W. C. BROAD, *Revista de la Universidad Industrial de Santander* **2**, 137 (1960).

<sup>14)</sup> S. P. SANGAL and A. K. DEY, *J. Sci. Industr. Res.* **21 B**, 600 (1962).

The stability constants were calculated by two different methods already mentioned and therefrom the free energy of formation was evaluated. In the following table the values are tabulated at the pH, mentioned against the systems, which was kept constant. The ionic strength could not be maintained at a constant level because the chelates have a tendency to precipitate out during attempts to swamp the systems with electrolytes.

Some tentative suggestions have been made about the possible position of the chelate ring in the Thoron complexes. It is well known that the donor properties of the azo group are weak, but azo groups containing a strong donor group in a position ortho to the azo group forms very stable chelate rings<sup>15</sup>). In Thoron there are the hydroxy- and the arsono-groups in ortho positions which make it suitable as a strong chelating agent. Both these groups are also capable of linking the metal ion by the removal of the proton. Thus the structure suggested involves the formation of two six membered rings as a result of chelation involving removal of two protons and the azo group.



The structures are further corroborated by the anionic nature of the lanthanum chelate and the neutral nature of the chelates of thorium, uranyl and palladium, as ascertained by adsorption experiments using columns of ion exchange resins.

### La-Chromotrope 2 B Chelate

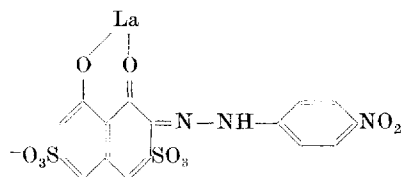
In continuation with the work on the metal chelates of p-nitrobenzene azochromotropic acid (Chromotrope 2-B; abbreviated as CTB) carried out in these laboratories, the chelate formation between lanthanum (III) and Chromotrope 2-B has now been investigated. Lanthanum forms a 1:1 chelate, which is pink in colour ( $\lambda_{\max}$  540 m $\mu$ ) and stable between pH 5.0–12.5. The values of the stability constants are summarised in the table below.

<sup>15</sup>) J. C. BAILAR JR., Chemistry of the coordination compounds Reinhold, New York, pp. 74, 754–760 (1956).

Table 3  
Stability of Lanthanum-CTB Chelate

Method	pH	log K	$\Delta F^\circ$ at 25°C (K Cals)
DEY et al.	6.0	$4.52 \pm 0.1$	$-6.3 \pm 0.2$
Mole Ratio	6.0	$4.94 \pm 0.15$	$-6.8 \pm 0.2$

The chelate was found to be neutral since it was not adsorbed either by (H) or (OH) varieties of ion exchange resins. It has been suggested that lanthanum is chelated to the oxygens of the hydroxyl groups, as follows:



This is in accordance with the observed neutrality of the chelate, as confirmed by adsorption using columns of ion exchange resins.

#### Pd-Chrome Azurol S chelate

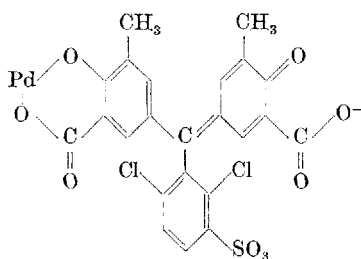
Considerable work has been done in these laboratories on the metal chelates of sulpho-dichloro hydroxy-dimethyl fuchson-dicarboxylic acid (Chrome Azurol S; abbreviated as CAS)<sup>16</sup>. The studies have now been extended and the formation of a violet coloured palladium chelate has been reported, for the first time. The chelate has a  $\lambda_{\max}$  585 m $\mu$  and is stable between pH 3.5–8.0. The composition of the chelate has been found to be 1:1 and the values of log K and  $\Delta F^\circ$  are shown in the table below.

Table 4  
Stability of the Palladium-Chrome Azurol S Chelate

Method	pH	log K	$\Delta F^\circ$ at 25°C (K Cals)
DEY et al.	4.0	$5.05 \pm 0.15$	$-7.0 \pm 0.2$
Mole Ratio	4.0	$4.75 \pm 0.10$	$-6.6 \pm 0.1$

<sup>16</sup> A. K. DEY, S. C. SRIVASTAVA, R. L. SETH, S. N. SINHA and S. P. SANGAL, VII. Int. Coord. Chem., Stockholm, Uppsala paper No. 7 B, pp. 330–332 (1962).

It has been suggested that chelation occurs between the phenolic oxygen and the adjacent carboxylic oxygen as follows:



This has further been confirmed by the anionic nature of the complex by adsorption of the colour by ion-exchange resin.

Observations have also been made on the possible use of the following reagents as chelatochromic indicators in the complexometric determination of thorium by ethylenediaminetetraacetic acid:

- (I) Quinizarin sulphonic acid<sup>17</sup>).
- (II) 1-(o-arsonophenylazo)-2-naphthol 3:6-disulphonic acid (Thoron)<sup>18</sup>).
- (III) Dimethylamino hydroxy phenoxazone carboxylic acid (Gallocyanine)<sup>19</sup>).
- (IV) Ammonium purpurate (Murexide)<sup>20</sup>).
- (V) p-nitrobenzene azo-chromotropic acid (Chromotrope 2-B)<sup>21</sup>).
- (VI) Sulpho-dichloro hydroxy-dimethyl fuchson dicarboxylic acid (Chrome Azurol S)<sup>22</sup>).

The effect of temperature, pH, dilution and interferences by added foreign ions have been studied and detailed conditions for the titrimetric procedure have been worked out.

<sup>17</sup>) S. P. SANGAL, *Chim. Analyt.* **46**, 138 (1964).

<sup>18</sup>) S. P. SANGAL, *Vij. Pari. Annu. Patrik.* **6**, 49 (1963).

<sup>19</sup>) S. P. SANGAL and A. K. DEY, *J. Indian chem. Soc.* **38**, 75 (1961).

<sup>20</sup>) S. P. SANGAL and A. K. DEY, *Talanta* **10**, 1115 (1963).

<sup>21</sup>) S. P. SANGAL and A. K. DEY, *Z. analyt. Chem.* **183**, 178 (1961).

<sup>22</sup>) S. P. SANGAL and A. K. DEY, *Z. analyt. Chem.* **178**, 415 (1961).

The author is thankful to Dr. A. K. DEY for his support throughout the progress of this work.

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Bei der Redaktion eingegangen am 24. August 1964.