



## **Dioximates of transitional metals. Syntheses, characterizations, applications**

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*Received: 22.08.2023 / Accepted: 23.08.2023 / Published: 20.12.2023*

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### **Abstract:**

Several derivatives of  $\alpha$  benzylidioxime with nickel, platinum and palladium are known to have been synthesized by Ciugaev, and later by F.P.Dwyer and D.P.Mallor. Recently, this reagent has found a wide use for the gravimetric determination of palladium and nickel, especially in semi-microanalysis, because the solubility of the respective chelate formed with  $\alpha$  benzylidioxime is lower, and the gravimetric factor has a more appropriate value than in the case of analog derivatives of dimethylglyoxime.

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**Keywords:** *dioximates, benzylidioxime, chelates*

## **1. INTRODUCTION**

The first combinations of trivalent cobalt with  $\alpha$  benzylidioxime were obtained in a crystalline state by I. Cambi and L. Malatesta. They synthesized a monobasic complex acid, namely hydrogen dibromo bis benzylglyoximate cobaltate  $H[Co(Dif)_2Br_2]$ , where Dif represents the benzildioximic  $\alpha$  group. A number of new monobasic complex acids of this class have been described.

It was also observed that acids of the type  $H[Co(Dif)_2X_2]$  hydrate in the presence of ammonia forming aquo non-electrolytes such as benzylglyoximate aquo cobalt acid (III)  $[Co(Dif)_2(H_2OX)]$  [7-9].

In the present article, we proposed to study the possibilities of introducing different organic aliphatic and aromatic amines into the inner coordination sphere of cobaltic benzyl dioximates.

## 2. MATERIALS AND METHODS

It was observed that by oxidizing a mixture consisting of  $\text{CoX}_2$ , different aromatic amines and benzyldioxime in a 1:3:2 molar ratio, cationic monovalent complexes of the type bis  $\alpha$  benzyldioximato cobaltic diamine are formed  $[\text{Co}(\text{Dif})_2(\text{Amin})_2]$ , (Table 1).

**Table 1.** Several properties of complex combination of  $[\text{Co}(\text{Dif})_2 \text{toluidine}]$

No	Complex combination	Molecular Weight calc	Yield %	Appearance	Analysis Co(III)	
					Calculated	Found
I	II	III	IV	V	VI	VII
1.	$[\text{Co}(\text{Dif})_2(\text{meta toluidine})_2]\text{Cl}$	787,2g	65%	Rhombic plates Macrocrystals Pink coloured	7,42	7,48
2.	$[\text{Co}(\text{Dif})_2(\text{orto toluidine})_2]\text{Br}$	831,7g	57,6%	Plates microcrystals Dark-yellow coloured	7,28	7,08
3.	$[\text{Co}(\text{Dif})_2(\text{meta toluidine})_2]\text{Br}$	831,7g	84%	Plates microcrystal redish coloured	6,86	7,08
4.	$[\text{Co}(\text{Dif})_2(\text{para toluidine})_2]\text{Br}$	831,7g	75%	Plates microcrystal Dark-yelow coloured	6,89	7,00
5.	$[\text{Co}(\text{Dif})_2(\text{orto toluidine})_2] \text{NO}_3$	813,8g	54,6%	Irregular plates Microcrystals, red-brick coloured	7,10	7,24

### *Analysis methods*

#### Preparation of $\alpha$ benzyldioxime:

80 g of NaOH are dissolved in 500 mL of water. After cooling, add a solution of 40 g of hydroxyl amine hydrochloride in 100 mL of water. After this, add 50 g of finely ground benzyl and also 25 mL of ethanol.

The benzyl dissolves slowly and forms a brown solution. After 3 days the untransformed solution is filtered and a strong current of CO<sub>2</sub> is bubbled through the solution.

The precipitated  $\alpha$  benzildioxime is filtered and purified by extraction with hot ethanol [10]. It has a melting point of 230 °C.

#### Obtaining [Co(Dif)<sub>2</sub>(o toluidine)<sub>2</sub>]Cl:

Place in a 100-150 mL round-bottomed flask, provided with an ascending refrigerant, 40 mL of methanol and 2.4 g of  $\alpha$ -benzyldioxime, 1.6 g of ortho toluidine and bring them to boil.

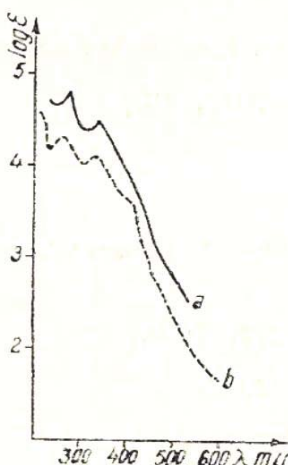
By boiling the solution, the dioxime slowly dissolves. After 10-15 minutes, add 1.18 g of CoCl<sub>2</sub>·6 H<sub>2</sub>O. The mixture is oxidized with 5 mL of H<sub>2</sub>O<sub>2</sub> 30 % in excess. The oxidant is added dropwise through the free side of the refrigerant, keeping the solution boiling continuously for 35- 40 minutes. The reddish solution becomes dark brown and a crystalline mass separates.

After cooling the solution, it is filtered, washed three times with 5-6 mL of cold methanol and air-dried.

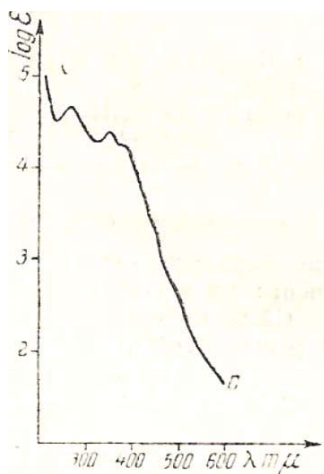
### 3. RESULTS AND DISCUSSION

#### *Spectrometric measurements*

The measurements were carried out at room temperature, at a concentration of 2.10-52.10<sup>-3</sup> mol/L in 96% methanol, 30-40 minutes after dissolving the samples. Under these conditions, the studied solutions follow the Lambert-Beer law, (Figures 1-2).



**Figure 1.** Visible and UV absorption spectra of the combinations [Co(Dif)<sub>2</sub>(orto toluidine)<sub>2</sub>]·NO<sub>3</sub> (a), [Co(Dif)<sub>2</sub>(meta toluidine)<sub>2</sub>]·NO<sub>3</sub> (b)



**Figure 2.** The visible and UV absorption spectrum of the combination  $[\text{Co}(\text{Dif})_2(\text{para toluidine})_2] \cdot \text{NO}_3$

#### 4. CONCLUSION

It was proved by the existing method of new complex cations such as  $[\text{Co}(\text{Dif})_2(\text{o toluidine})_2]^-$ ,  $[\text{Co}(\text{Dif})_2(\text{meta toluidine})_2]^-$ ,  $[\text{Co}(\text{Dif})_2(\text{p toluidines})_2]^-$ , obtaining new complex combinations.

The ortho, meta and para derivatives of toluidine are positional isomers, with very similar physical and chemical properties

Through spectrophotometric measurements, conclusions were drawn on the structure of these substances, as well as on the nature of the chemical bonds in their molecules.

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