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RESEARCH ON BENZO- AND NAPHTHAZOLES

XIV. Nickel and Copper Complexes of Formazans of the Benzimidazole Series*

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Nickel and copper complexes of asymmetric 1-(1'-alkylbenzoimidazolyl-2')-3-methyl-5-arylformazans and symmetric 1, 5-di(1'-alkylbenzoimidazolyl-2')-3-alkylformazans are prepared, and their absorption spectra in the visible region are measured. Some views regarding the structures of the complexes are considered.

The symmetric 1, 5-dibenzoimidazolylformazans [2] and asymmetric 1-benzoimidazolyl-5-arylformazans [1] that have been prepared are excellent complexing agents with many metals, and this connects them with the 1, 5-diarylformazans [3, 4]. We have now prepared and investigated the complex compound obtained from nickel and divalent copper

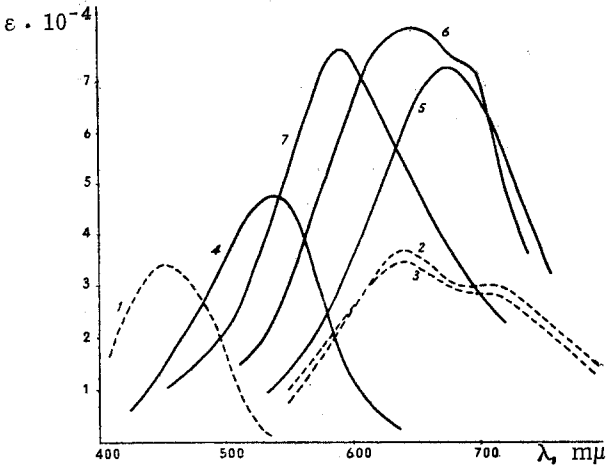


Fig. 1. Absorption spectra: 1) 1-(1'-benzylbenzoimidazolyl-2')-3-methyl-5-p-tolylformazan; 2) complex of that formazan with $CuCl_2$ (VII); 3) same complex after washing a chloroform solution with water; 4) 1, 5-di(1'-benzylbenzoimidazolyl-2')-3-methylformazan; 5) complex of that formazan with $CuCl_2$ (XIII); 6) complex XIII after washing a chloroform solution with a water solution of $CuCl_2$; 7) complex XIII after washing a chloroform solution with water.

salts and asymmetric and symmetric formazans of the benzoimidazole series. The complexes were prepared by mixing an alcohol or acetone solution of the salt with a solution of the formazan in the same solvent, when the complexes precipitated as dark crystals. The composition of the complexes can be derived from the results of elementary analysis.

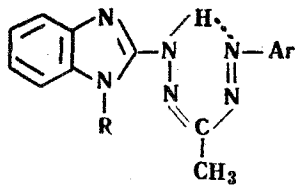
With nickel nitrate, the asymmetric 1-(1'-benzylbenzoimidazolyl-2')-3-methyl-5-phenylformazans, with a p-nitro- or o-hydroxy group in the benzene ring, gave the complexes I, II, composition 2F + 1Ni (see Table 1). The formazan with an ortho- carboxyl group, forms the complex III, composition 1F + 1Ni, in which the carboxyl apparently participates in complex formation. The complexes of 1-(1'-alkylbenzoimidazolyl-2')-3-methyl-5-arylformazans with cupric chloride are more complex in composition, since the benzoimidazole rings are apparently able to act as ligands for additional molecules of $CuCl_2$. The compositions of the complexes of the formazans with various groups in the aryl portion (compounds IV, V, VII-IX), correspond to the formula 2F + 1Cu + 1$CuCl_2$. When the complexes are recrystallized from alcohol or acetone, a molecule of $CuCl_2$ is not lost, nor is it on shaking a chloroform solution of the complex with water, as is evident in the case of complex VII from the absorption spectra in the visible region (Fig. 1). Like ortho- carboxyl-containing arylformazans [5], 1-(1'-benzylbenzoimidazolyl-2')-3-methyl-5-o-carboxyphenylformazan, forms a complex VI of composition 1F + 1Cu. In this reaction, intermolecular coordination probably occurs (imidazole ring nitrogen → metal), as is indicated by the inability of the complex VI to add to another molecule of $CuCl_2$. A hypothetical structure for the complex is shown in Fig. 2.

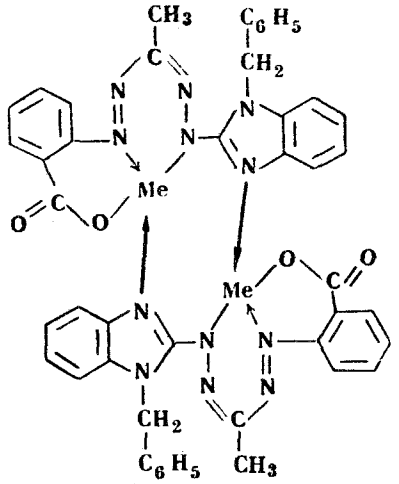
With nickel, symmetric 1, 5-di(1'-benzylbenzimidazolyl-2')-3-methylformazan gives the complex X, resembling the diphenylformazan complexes [3]. The composition of this complex is 2F + 1Ni. On the other hand the analytical results for complexes of the same formazan with various copper salts (acetate, nitrate, chloride), shows that complexes XI-XIII are more complex in composition, 2F + 1Cu + 2$Cu(A)_2$, i. e., the complex can retain 2 additional molecules of copper salt. To ascertain to what extent this ability of 1, 5-dibenzylimidazolylformazans to add the copper salt is a function of the groups at the 1-position in the imidazole rings and the 3- position in the formazan ring [and in what way it is connected to the ability of the starting formazan to hold a component (water or alcohol of crystallization)], com-

*For Part XIII see [1].

Table 1

Complex Compounds from 1-(1-Alkylbenzoimidazolyl-2)-3-methyl-5-arylformazans



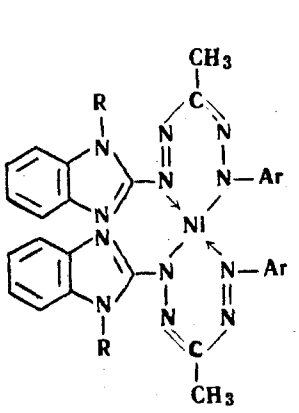


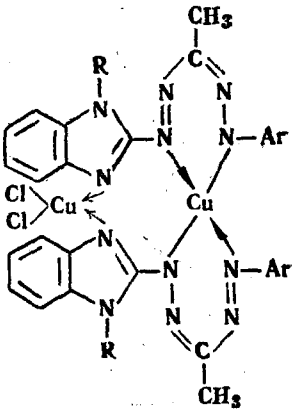
Compound no.	R	Ar	Salt used	Mp, °C	Color and shape of crystals	λ_{max}, mμ	ε · 10⁻⁴	Formula	Found, %			Calculated, %			Yield of the complex, %
									N	Cl	Ni, Cu	N	Cl	Ni, Cu	
I	$CH_2C_6H_5$	p-$C_6H_4NO_2$	$Ni(NO_3)_2 \cdot 6H_2O$	250—254	Brown needles	672	6.36	$(C_{22}H_{18}N_7O_2)_2Ni$	22.14	—	Ni 6.58	22.17	—	Ni 6.63	70
II	$CH_2C_6H_5$	o-C_6H_4OH	„	>300	Dark brown needles	664	5.54	$(C_{22}H_{19}N_6O)_2Ni$	19.56	—	Ni 7.08	20.35	—	Ni 7.11	90
III	$CH_2C_6H_5$	o-C_6H_4COOH	„	>300	Brown needles	536	1.54	$C_{23}H_{18}N_6O_2Ni$	17.95	—	Ni 12.30	17.91	—	Ni 12.51	90
IV*	$CH_2C_6H_5$	p-$C_6H_4NO_2$	$CuCl_2 \cdot 2H_2O$	233	Brown plates			$(C_{22}H_{18}N_7O_2)_2Cu \cdot CuCl_2$	19.67	7.25	Cu 12.24	19.17	6.93	Cu 12.43	65
V	$CH_2C_6H_5$	o-C_6H_4OH	„	188—189	Brown needles with a green reflex	532	3.64	$(C_{22}H_{19}N_6O)_2Cu \cdot CuCl_2$	17.15	7.44	Cu 13.19	17.40	7.34	Cu 13.16	60
VI	$CH_2C_6H_5$	o-C_6H_4COOH	„	227	Black needles with a violet reflex	>750		$C_{23}H_{18}N_6O_2Cu$	17.98	—	Cu 13.55	17.72	—	Cu 13.40	50
VII	$CH_2C_6H_5$	p-$C_6H_4CH_3$	„	207—208	Bluish-green needles with a violet reflex	642 710	3.73 3.05	$(C_{23}H_{21}N_6)_2Cu \cdot CuCl_2$	17.96	7.47	Cu 13.05	17.48	7.38	Cu 13.22	70
VIII	CH_3	p-$C_6H_4CH_3$	„	189—190	Black needles	640 710	2.02 1.64	$(C_{17}H_{17}N_6)_2Cu \cdot CuCl_2$	20.45	8.52	Cu 15.57	20.77	8.76	Cu 15.71	70
IX	$CH_2C_6H_5$	p-C_6H_4Cl	„	207	Brown plates with a bronze reflex	646 722	3.86 3.11	$(C_{22}H_{18}N_6Cl)_2Cu \cdot CuCl_2$	16.30	13.73	Cu 12.53	16.79	14.15	Cu 12.69	56

*Substance has low solubility in chloroform.

plexes were prepared from various 1, 5-dibenzylimidazolylformazans and $CuCl_2$.

Table 2 shows that complexes of $CuCl_2$ with various symmetric formazans have varying compositions, XIII, and XVI holding two molecules of $CuCl_2$, XV, XVII, and XVIII containing $CuCl_2$ + 2HCl, and XIV, $2CuCl_2$ + HCl. At present it is difficult to decide what connection there is between the character of the alkyl groups at the 1'- or 3- position and complex formation. It is evident that the various radicals, by altering the basicity of the nitrogen atoms in the imidazole and formazan rings, in some cases bring about addition of $2CuCl_2$, and in others of $CuCl_2$ + 2HCl.



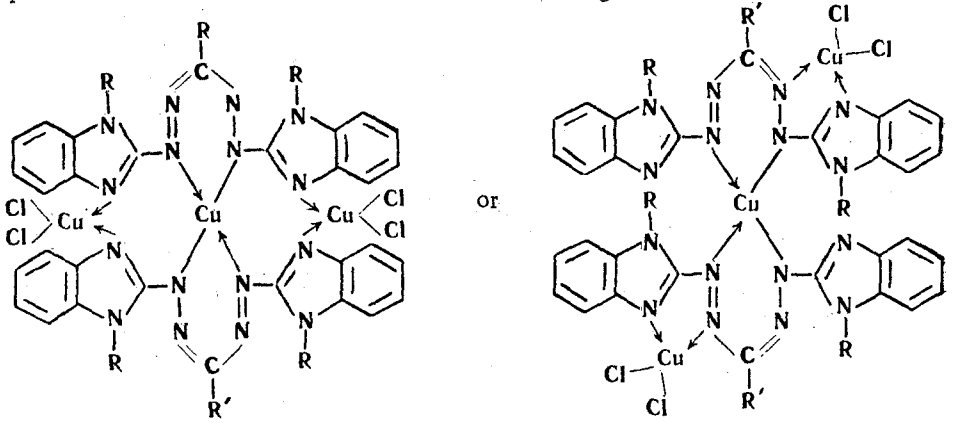


I R=$CH_2C_6H_5$; Ar=p-$C_6H_4NO_2$
II R=$CH_2C_6H_5$; Ar=o-C_6H_4OH
III Me=Ni
VI Me=Cu

IV R=$CH_2C_6H_5$, Ar=p-$C_6H_4NO_2$
V R=$CH_2C_6H_5$, Ar=o-C_6H_4OH
VII R=$CH_2C_6H_5$, Ar=p-$C_6H_4CH_3$
IX R=$CH_2C_6H_5$, Ar=p-C_6H_4Cl
VIII R=CH_3, Ar=p-$C_6H_4CH_3$

Fig. 2

The complex XIII is assumed to have the structure shown in Fig. 3.



R=$CH_2C_6H_5$; R'=CH_3

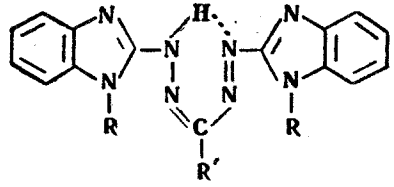
Fig. 3

It was observed that these complexes, unlike those from asymmetric formazans, are unstable, and that on recrystallizing from chloroform they partly lose $CuCl_2$, as indicated by the analytical data for chlorine. (Table 2 gives analytical data for complexes which have not been recrystallized.) These complexes are rather sparingly soluble in chloroform, but on shaking with a mixture of chloroform and water, they become quite soluble in the chloroform, indicating that the composition of the complex has changed. After repeated washing with water, a chloroform solution of the complex XIII gave, on evaporation, a compound approximately corresponding in composition to 2F + 1Cu, but it was not possible to completely remove the chlorine from the complex. Unlike the starting material, the resultant compound is readily soluble in organic solvents. Figure 1 shows the changes in absorption spectra curves of the complex XIII when chloroform solutions are washed with aqueous $CuCl_2$ solution and water. Washing with $CuCl_2$ solution probably leads to partial loss, while washing with water leads almost to complete loss of a molecule of $CuCl_2$ from the complex.

Furthermore, the complex of a symmetric formazan with nickel, X, exhibits a capacity to add cupric chloride and give a new complex with the composition 2F + Ni + $2CuCl_2$ (from data of chlorine analysis). Here, obviously, nickel is not displaced by copper, since the resultant complex is not identical with the complex XIII. Figure 4 shows the changes in absorption curves of the nickel complex on filling it with $CuCl_2$ and then washing it out with water.

Table 2

Complex Compounds from 1, 5-Dibenzoimidazolylformazans



Compound no.	Starting formazan			Salt taken	Mp, °C (with decomp)	Appearance of crystals	λ_{max}, mμ	ε · 10^{-4}	Formula	Found, %			Calculated, %			Yield of the complex, %
	R	R_1	Formula							N	Cl	Cu	N	Cl	Cu	
X*	$CH_2C_6H_5$	CH_3	$C_{30}H_{26}N_8 \cdot 2H_2O$	$Ni(NO_3)_2 \cdot 6H_2O$	>300	Bluish-green needles		—	$(C_{30}H_{25}N_8)_2Ni$	21.69	—	6.00 (Ni)	21.27	—	5.57 (Ni)	90
XI	„	„	„	$Cu(CH_3COO)_2 \cdot H_2O$	233—235	Golden brown needles	618 664	8.81 11.18	$(C_{30}H_{25}N_8)_2Cu \cdot 2Cu(CH_3COO)_2$	15.09	—	13.98	15.76	—	13.40	75
XII*	„	„	„	$Cu(NO_3)_2 \cdot 5H_2O$	217 (explodes)	Golden brown leaflets	—	—	$(C_{30}H_{25}N_8)_2Cu \cdot 2Cu(NO_3)_2$	18.36	—	14.10	19.53	—	13.29	98
XIII	„	„	„	$CuCl_2 \cdot 2H_2O$	203—204	Brown plates	672	7.27	$(C_{30}H_{25}N_8)_2Cu \cdot 2CuCl_2$	16.12	10.33	14.65	16.88	10.68	14.35	67
XIV	„	H	$C_{29}H_{24}N_8 \cdot 4H_2O$	„	183—184	Brown plates	684	6.22	$(C_{29}H_{24}N_8)_2Cu \cdot 2CuCl_2 \cdot HCl$	16.68	13.46	14.69	16.76	13.26	14.26	75
XV	„	n-C_3H_7	$C_{32}H_{30}N_8 \cdot 2H_2O$	„	212—213	Dark brown plates	670	6.36	$(C_{32}H_{30}N_8)_2Cu \cdot CuCl_2 \cdot 2HCl$	17.06	10.46	9.72	16.95	10.72	9.61	80
XVI*	H	CH_3	$C_{16}H_{14}N_8$	„	>300	Dark brown plates	—	—	$(C_{16}H_{13}N_8)_2Cu \cdot 2CuCl_2$	22.88	13.90	18.80	23.17	14.66	19.71	61
XVII*	CH_3	CH_3	$C_{18}H_{18}N_8 \cdot 2H_2O$	„	240—242	Blackish-violet	666	—	$C_{18}H_{17}N_8)_2Cu \cdot CuCl_2 \cdot 2HCl$	21.93	14.64	13.34	23.30	14.74	13.21	87
XVIII	C_2H_5	CH_3	$C_{20}H_{22}N_8 \cdot H_2O \cdot C_2H_5OH$	„	192—193	Brown plates with green reflex	667	5.60	$(C_{20}H_{21}N_8)_2Cu \cdot CuCl_2 \cdot 2HCl$	21.17	13.11	12.62	22.02	13.93	12.48	96

*Substance poorly soluble in chloroform.

When preparing complexes from salts of divalent copper, no cases of reduction of the copper to the monovalent state and oxidation of part of the formazan, which occurs with readily oxidized arylformazans [6], were observed.

Experimental

Complex of 1-(1'-benzylbenzoimidazolyl-2')-3-methyl-5-p-tolylformazan with $CuCl_2$ (VII). 0.001 mole of the formazan was dissolved in 15 ml acetone and mixed with a warm solution of 0.0015 mole $CuCl_2 \cdot H_2O$ in 15 ml acetone. Evaporation of the dark green solution gave about half of the crystalline complex, which was recrystallized from alcohol. The complexes of the asymmetric formazans I-IX with $Ni(NO_3)_2$ and $CuCl_2$ were prepared similarly.

Complex of 1,5-di(1'-benzylbenzoimidazolyl-2')-3-methylformazan with nickel (X). 0.002 mole of the formazan was dissolved in 200 ml alcohol (or 50 ml acetone) and mixed with a solution of 0.003 mole $Ni(NO_3)_2 \cdot 6H_2O$ in 20 ml dilute (50%) alcohol plus 1 ml concentrated NH_4OH. The dark blue solution was boiled for a few minutes, and then half of the alcohol distilled off. The solution, on cooling, deposited crystals of the complex, readily soluble in alcohol, acetone, and chloroform, insoluble in benzene.

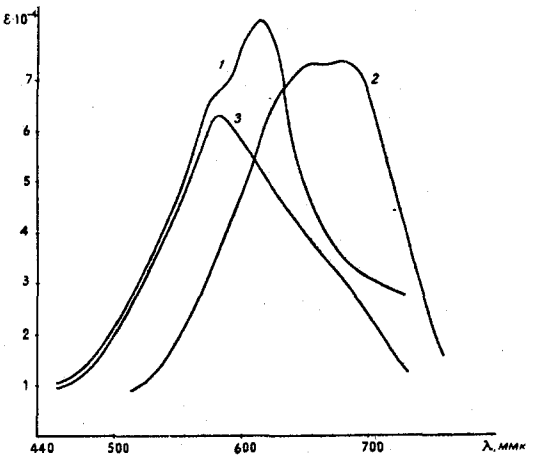


Fig. 4. Absorption spectra: 1) Complex of 1,5-di(1'-benzylbenzoimidazolyl-2')-3-methylformazan with Ni (X); 2) Complex prepared from X and $CuCl_2$ (2F + Ni + $2CuCl_2$); 3) The same, after washing with water.

Reaction of the complex X with cupric chloride. A solution of 0.001 mole $CuCl_2 \cdot 2H_2O$ in 20 ml acetone was added to 0.0005 mole nickel complex X in 50 ml acetone, and the whole heated to boiling. On cooling and standing, brown plates with a yellowish reflex precipitated. Yield 30-40%, mp 190-191°. Found: Cl 10.46%. Calculated for $(C_{30}H_{25}N_8)_2 \cdot 2CuCl_2$: Cl 10.72%.

Complex of 1,5-di(1'-benzylbenzoimidazolyl-2')-3-methylformazan with $CuCl_2$ (XIII). A solution of 0.001 mole of the formazan in 30 ml acetone was mixed with a solution of 0.003 mole $CuCl_2 \cdot 2H_2O$ in 20 ml acetone. Crystals of the complex soon precipitated from the dark green solution. The complexes of the other symmetric formazans with $CuCl_2$ (XIV-XVIII) were prepared similarly. 1,5-di(benzylbenzoimidazolyl-2')-3-methylformazan is poorly soluble in acetone, consequently the complex XVI was prepared in methanol.

Washing-out complex XIII with water. 0.3 g complex XIII was dissolved in 100 ml chloroform. The dark green solution was repeatedly shaken (20 times) with fresh portions of distilled water (70-100 ml). The chloroform solution became blue, then bluish violet. After evaporating off the chloroform, we obtained 0.1 g of a crystalline substance mp 140-150° (decomp), readily soluble in acetone, alcohol, and chloroform. Found: Cu 6.31; Cl 3.98%. Calculated for $[(C_{30}H_{25}N_8)_2Cu$: Cu 6.0%. Calculated for $(C_{30}H_{25}N_8)_2Cu \cdot HCl$: Cu 5.8; Cl 3.05%].

Copper and nickel in the complexes were determined with trilon. The visible spectra were measured with an SF-10 spectrophotometer in chloroform, solution concentration 10^{-4} M.

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