METAL COMPLEXES OF PSEUDOAROMATIC NITROGEN-CHELATES

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In our previous investigations [1], [2] the nature of the N–H...N bridge in pseudoaromatic chelates (six-membered chelate systems containing two conjugated double bonds) has been examined. Reactions brought about by extinction of the hydrogen bridge were examined on ⍺-benzol-azo-N-phenyl-β-naphtyl-amin (further on as BPhNA) as model compound and their substituted derivatives with kinetic and spectroscopic methods. In this paper metal complexes of BPhNA and their decomposition reactions will be treated.

We prepared the metal complexes Co(II), Ni(II) and Cu(II) of BPhNA which appeared to be black coloured, well crystallized substances with high melting points. They are found to be insoluble in polar solvents and, even in apolar solvents they show a poor solubility. They are stable against alkali but on the effect of acids, even of acetic acid, they decompose into their components.

On the basis of some physico-chemical properties and data of analysis (Table 3) these metal compounds have to be considered as neutral, tetracoordinated complexes which may be written by the general formula $M^{II}(BPhNA)_2$.
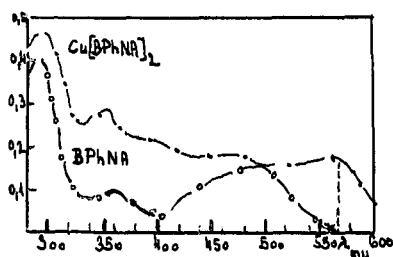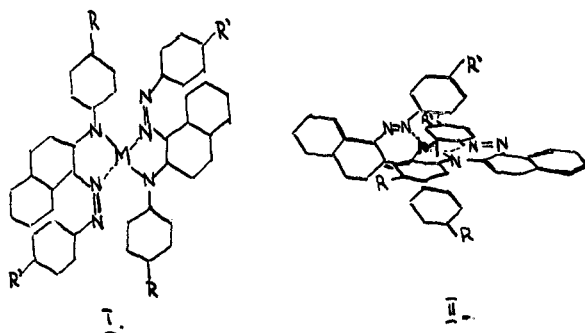
However, the structural formula of our metal complexes is a problematical one, the following alternatives being given for it. The structure may be
1.) a five-membered, energetically less favourable metal chelate in which a co-planar arrangement would be possible, (formula I.) or
2.) a six-membered, energetically more advantageous pseudo-aromatic metal chelate, in which, however, by the steric hindrance of the aryl-radicals any coplanar arrangement is prevented and only a tetrahedral (distorted or regular) structure would be permitted (formula II.).

A comparison between the absorption spectra of the H-chelate and the metal chelates in the ultraviolet and visible region (Fig. 1) shows that
1.) in the whole region the absorption curve of the metal chelate is running over the curve of the H-chelate,
2.) while the former shows an extensive absorption with a wavelength of 570 mμ, for the latter (no absorption could be observed) at this wavelength,
3.) within 24 hours the absorption curve of the metal chelate in benzene solution will run into the absorption curve of the H-chelate on the effect of acetic acid.

On the basis of those observations photometrical methods seemed to be the most convenient for an examination of this decomposition reaction of metal complexes. The alteration of extinction on the effect of acetic acid has been tested in benzene solution of the complexes at 570 mμ. There has been determined a kinetics of second order and from the experimentally observed half-

periods the rate constants were computed. Rate constants of the BPhNA com-
plexes of cobalt, nickel and copper are summarized in the first row of Table 1.

In order that the effect arising from the electron shift of the ligands in the
decomposition reaction of metal complexes could be taken into consideration,
partly the metal complexes BPhNA substituted by electron-repelling methyl
groups and partly metal compounds substituted by electron-attracting chlorine
atoms have been prepared. The position of substituents to the N atoms of the
basis compound is shown in para position by R and R' in the formulae I. and
II. Rate constants for metal complexes of ligands with larger or smaller electron
densities are also given in Table 1.

Table 1

Rate constants of decomposition of the metal chelates $M(BPhNA)_2$ in units of $L.mol^{-1}.min^{-1}$ at $18^{o}C$.

	$Co(BPhNA)_2$	$Ni(BPhNA)_2$	$Cu(BPhNA)_2$
R=R* = H	0,44	0,66	278
R=R = CH$_3$	0,66	0,77	696
R=R* = Cl	0,39	0,46	147

Some conslusions for the nature of the decomposition reaction and the structure of the metal complexes may be drawn from a comparison of data of the reaction kinetics.

With all the three metals the rate of decomposition reaction follows the order of $CH_3 > H > Cl$ as a function of the substituents, which means that the rate constant in each metal complex shows a monoton increase on an augmentation of the electron density in the N atoms joined to the metal. However, the values of the rate constants are not independent of the metal components either. While the constants of nickel and cobalt could be found close to each other, a difference of 2–3 order of magnitude occurs between the constants of copper and the other metals. So it is possible that the rate determining elementary process would be an ″exchange process″ associated with protonation in which the intensity of the metal–nitrogen bond will also be shown. However, it is surprising that the order of rate is decreasing in the direction of $Cu^{2+} \gg Ni^{2+}Co^{2+}$ as a function of the metals, whilst on the basis of the generally accepted Irving-Williams stabilizing sequence [3] just the opposite should be expected.

Taking, however, into consideration that the Irving-Williams statement is generally referred to complexes without steric hindrances, just from the deviation in the sequence mentioned above, the conclusion may be drawn that, a strained tetrahedral structure will be shown by our complexes (Formula II.) This view is supported by our investigations carried out on previously [4] described nickel (II) and copper (II) complexes of sterically not hindered α-benzolazo – β– naphtol (BAN). The rate constants of the decomposition occurring of acetic acid are shown in Table 2.

Table 2

Rate constants of decomposition of the complexes $M(BAN)_2$ is units of $l. mol^{-1}. min^{-1}$ at $18^{o}C.$

	Ni(II)	Cu(II)
$M(BAN)_2$	70	0,3

Since no spatial hindrance for a more stable coplanar arrangement exists, in agreement with the Irving-Williams order, the copper compounds were practically stable against acetic acid under identical conditions when the decomposition of the nickel compound could be still measured.

On the basis of the ligand-field [5] theory Co^{2+} and Ni^{2+} with the electron structures d^7 and d^8 appear to be tetrahedral in their tetracoordinated complexes in »spin-free state«, while Cu^{2+} with the electron structure d^9 is forming relatively the most stable bonds with planar tetragonal hybrid orbitals. With such configurations the charge-increase in the nucleus from cobalt to copper would imply an increase in stability. When on the copper complex a tetrahedral structure is constrained a relative decrease of the stability may be expected. An interesting picture occurs with »spin-paired« structures. For the structure of cobalt-, nickel- and copper-complexes in »spin-paired state«, bonds of dsp^2 tetragonal orbitals are exclusively assumed, when again a mono-ton increase of the stability is incident to the nuclear electrical charge. In the case of copper complexes, a d-electron is induced upon a p-orbit by which, however, the bonds of tetragonal ligands are not disturbed. When the formation of tetragonal planar hybrid orbitals is prevented by an external constraint, which in the case of our investigated complexes is achieved by steric hindrances of the aryl-radicals, then by the tetrahedral structure some other hybrid orbitals would presumably be induced to occupy the bonding electrons of the central atom. Among the eight kinds of tetracoordinated hybrid states computed theoretically by Kimbal [6] the formation of the distorted tetrahedral hybrid system of dp^3 will be the most probable one in this case. Then, a relatively smaller decrease in the stability of cobalt-and nickel-complexes would appear: in copper-complexes, however, the excited electron will be forced to transfer from the nonbonding d-orbit to the s-orbit. Since by the s-electron a larger repulsing effect is exerted on the tetrahedral ligands, that may be the cause of the high decrease in stability.

We want to continue our investigations and magnetic measurings are planned to clarify this problem.

Experimental

Preparations of Hydrogen Chelates

were carried out according to Zincke and Lawson's method [7] and our modifications [1] respectively.

Preparations of Metal Chelates

To two moles of hydrogen chelates dissolved in butanol (1g/50 ml) one mole of corresponding metal (II) acetate in 50 per cent aqueous methanol (1g/70 ml) was added and refluxed for thirty minutes. The obtained dark coloured crystals were recrystallized by dissolving in hot benzene (1g/500 ml) and precipitated with twice volume of methanol. Analytical data are summarized in Table 3.

Table 3

Melting point and data of analysis of the metal complexes BPhNA. Theoretical values in parenthesis.

	Co(BPhNA)$_2$	Ni(BPhNA)$_2$	Cu(BPhNA)$_2$
R = R' = H	m.p. 286° N /11,94/ 12,29 Co /8,39/ 8,30	m.p. 304° N /11,98/ 11,85 Ni / 8,35/ 7,99	m.p. 263° N /11,89/ 11,99 Cu/ 8,95/ 8,72
R = R' = CH$_3$	m.p. 350° N /11,08/ 11,11 Co / 7,76/ 7,18	m.p. 350° N /11,05/ 11,08 Ni / 7,73/ 7,69	m.p. 260° N /11,20/ 11,10 Cu / 8,47/ 8,40
R = R' = Cl	m.p. 325° N / 9,90/ 9,64 Co / 7,01/ 6,79	m.p. 317° N /10,0/ 9,90 Ni / 6,98/ 7,16	m.p. 274° N / 9,94/ 9,65 Cu / 7,50/ 7,63

Kinetic investigations

To a 10^{-4} mole/l benzene solution of metal complexes benzene acetic acid solution of identical volume has been added and the change of absorbancy measured with Pulfrich photometer (filter S57, 2 cm cells) at 18° C. To obtain well measurable rates of identical order of magnitude the concentration of acetic acid must be 10^{-2} mole/l in the case of copper complexes and one mole/l in nickel and cobalt complexes.

Table 4. demonstrates the half-periods of reaction (in minutes) found experimentally.

Table 4

	Co/BPhNA/$_2$	Ni/BPhNA/$_2$	Cu/BPhNA/$_2$
M/BPhNA/$_2$: HOAC	$1:10^2$	$1:10^2$	$1:10^2$
R = R' = H	3,15	2,10	0,50
R = R' = CH$_3$	2,10	1,80	0,20
R = R' = Cl	3,55	3,00	0,95

Rate constants computed from these data on the basis of the kinetic second order are given in Table 1. The assumption of second order is supported by investigations carried out on Cu/BPhNA/$_2$ complexes /R=R' = CH$_3$/ substituted by methyl radicals reacting with the highest rate. This compound decomposes already with fourfold excess of acid in measurable rate. The mean values (732 min^{-1}. mol^{-1}) of the constants computed with the formula of the second order rate constant is in fairly good agreement with the constant (696 min^{-1}.mol^{-1}) comput from the half-period of decomposition with a 100-fold exess of acid.

Similarily determined rate constants of decomposition of the metal chelates M(BAN)$_2$ are given in Table 2. The authors want to thank professor G. Schay for his interest and invaluable advice in this work. Thanks are also due to Mrs. Gy. Kerecsényi and Miss M. Barkics for carrying out the analysis.

References

[1] Messmer, A., J. Várady, I. Pintér: Magyar Tud.Akad.Kém.Tud.Oszt. Közl. 9, 329 (1957).

Acta Chim.Hung. 15, 183 (1958).

[2] Messmer, A., O. Szimán: Magy.Kém.Folyóirat 64, 290 (1958).

[3] Irving, H., R.J.P. Williams: J. Chem. Soc. 1953, 3202.

[4] Charrier, B., A. Beretta: Gazzetta 56, 869 (1926).

[5] Gillespie, R.J., R.S. Nyholm: Quart. Rev. 11, 360 (1957).

[6] Kimball, G.E.: J. Chem. Phys. 8, 188 (1940).

[7] Zincke, T., A.T. Lawson: Ber. 20, 1168 (1887).