

Synthesis, characterization, spectroscopic and crystallographic investigation of metal complexes of N-benzyl-N-nitrosohydroxylamine

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ABSTRACT

New metal complexes of N-benzyl-N-nitrosohydroxylamine (BNHA) are isolated and characterized by elemental analysis, IR and UV-VIS spectroscopy. Spectrophotometric titration of aqueous solutions of BNHA by salts of some transition metals allowed to calculate the composition and formation constants of the metal complexes. The crystal structure of Cu(BNHA)₂ is studied by X-ray diffraction. The Cu atom is coordinated by four O atoms of two bidentate ligands, which close 5-membered chelate rings. The N-O (1.306 Å - 1.320 Å) and N-N (1.274 Å and 1.275 Å) bond lengths indicate that π electrons are delocalized over the chelating groups. Complexes form stacks with intermolecular Cu...N contacts equal to 3.118 Å and 3.306 Å.

Keywords: N-Benzyl-N-Nitrosohydroxylamine; BNHA; Potassium Salt; Complex Compounds; IR; UV-Visible; Single Crystal X-Ray Diffraction; Formation Constants

1. INTRODUCTION

The feature of chelate-forming derivatives of N-nitrosohydroxylamines is the possibility to form stable complexes with the metallic ions of various natures (for example, Al and Pd).

The ammonium salt of N-nitroso-N-phenylhydroxylamine, is a well known (as cupferron) analytical reagent and it was very popular especially during the classical period of analytical chemistry [1-3]. This ligand is known to form complexes with many metals but only few of them have been structurally characterized [4-15].

Recently it was shown that many ortho-substituted N-nitroso-N-oxybenzenamines are good NO donors for both *in vitro* and *in vivo* assays [16]. As the major bio-

logical functions of NO include controlling blood pressure, smoothing muscle tone and platelet aggregation, and participating in neuronal synaptic transmission, Thus, the development of new substances which are potential NO donors and studies of their structure and properties are current challenges facing medicinal and synthetic chemists.

In addition, cupferron is a biologically active compound, known to display carcinogenic, genotoxic, mutagenic and DNA-damaging effects [17,18]. The knowledge of the chemistry of cupferron and its analogues containing N-nitrosohydroxylamine fragments could contribute to a better understanding of the interaction of nitrogen oxide with metal centers of biologically important species.

Here we report the isolation and characterization of some transition metal complexes with N-benzyl-N-nitrosohydroxylamine (BNHA).

2. EXPERIMENTAL

2.1. Measurements

The electronic spectra in the 200 - 800 nm range were obtained on a Varian spectrophotometer "Cary 50 scan", using aqueous 10⁻⁴ M solutions. IR spectra were recorded in KBr on a Varian "Excalibur HE 3100" FT spectrophotometer. Single crystal was characterized by a Bruker APEX II diffractometer. All the chemicals are commercially available and they were used without further purification. All the solvents were dried using standard methods before use.

2.2. Synthesis of K(BNHA) and Transition Metal Complexes

K(BNHA) and Cu(BNHA)₂. The synthesis was performed according to the procedure described in [19]. A solution of benzylmagnesium chloride was prepared

from magnesium (24.3 g, 1 mol) and benzyl chloride (126.7 g, 1 mol) in the dry Et₂O (800 mL). The NO gas was bubbled through the solution under vigorous stirring and cooling at such a rate that NO was almost entirely absorbed. The NO flow rate and the degree of its absorbance were controlled by the comparison of the rate of NO bubbling through the bubble vessel filled by NaOH at the outlet of the reactional vessel. The reaction mixture temperature was maintained in the range -20°C - -30°C. A pasty solid was separated and encumbered stirring. After the period of a rapid NO absorption (1 h), stirring was continued in an NO atmosphere for 0.5 h until the NO absorption was completed, with a gradual increase in temperature to 0°C. The reaction mixture was purged with Ar to avoid side reactions involving both NO and the Grignard reagent, cooled to -10°C, and then a mixture of MeOH (50 mL) and Et₂O (50 mL) was gradually added. The reaction mixture was poured into 700 mL of water, acidified with 5 M HCl, the ethereal layer was separated, and the aqueous layer was extracted with Et₂O (100 mL × 3). The combined extracts were washed with an excess of 10% KOH. The aqueous layer was neutralized with 5 M HCl until pH 4. The precipitate of N-benzyl-N-nitrosohydroxylamine was washed with water. The wet product was dissolved in the appropriate quantity of 10% KOH, so that the pH value reached 8 - 9. The mixture was concentrated in vacuo, the residue (108 g) was crystallized from EtOH (200 mL), and dried in air. Yield 79.1 g (39.7%), colorless plates, dehydration temperature 110°C - 115°C, m.p. 211°C - 214°C (dec.). Upon heating (1 h) in vacuo at 110°C - 145°C, a sample of the air-dried salt (10.5547 g) lost 0.4838 g, *i.e.*, 0.507 mol of H₂O per one mol of the hydrated salt was removed. Filter liquor was concentrated to 50 mL, and the additional air-dried product (14.2 g) was precipitated with Et₂O (250 mL). The overall yield of K(BNHA) was 93.3 g (46.8%). The treatment of the combined filtrate and wash

liquors with CuSO₄ additionally gave 9.1 g (5%) of Cu(BNHA)₂ (m.p. 157°C - 158°C (dec.)). The overall yield of K(BNHA) and Cu(BNHA)₂ 51.8%.

2.3. Transition Metal Complexes of BNHA

The above mentioned complexes were prepared by the reaction of the corresponding metal chloride with K(BNHA). In a typical reaction, an aqueous solution containing 1 mmol of MCl₂·xH₂O was slowly mixed with 2 mmol of the K(BNHA) under vigorous stirring. The obtained precipitates were collected and re-crystallized from ethanol. Yields 50% - 70%.

The formulae of the obtained complexes are derived from the elemental analysis and presented in the **Table 1**.

2.4. Electronic Spectroscopic Measurements

Spectrophotometric titration of solutions of K(BNHA) with the solutions of metal salts in water was carried out in neutral and alkaline media. Based on the results of titration, the saturation curves were drawn for several wavelengths, and the metal-to-ligand ratios were calculated. The formation constants of metal complexes were determined by the procedure described by Beck & Nadypal [20].

2.5. X-Ray Data Collection and Structure Determination

Light blue needles of Cu(BNHA)₂ suitable for X-ray data collection were obtained while re-crystallisation from ethanol. The diffraction data were collected on a Bruker APEX-II CCD diffractometer at room temperature and processed using the Bruker software [21]. The structure was solved by the direct method. The positions of the hydrogen atoms were calculated. The non-hydrogen atoms were refined in the anisotropic approximation, and the hydrogen atoms were refined within the riding model.

Table 1. Chemical analysis (calculated/observed) and empirical formulae of the isolated complexes.

No.	Structure	Formula	% M	% C	% H	% N	M
1	K(BNHA)	C ₇ H ₇ KN ₂ O ₂		44.19/44.23	3.71/3.44	14.73/14.92	190.24
2	Cu(BNHA) ₂ ¹	C ₁₄ H ₁₄ CuN ₄ O ₄	17.37/17.08	45.96/45.25	3.86/3.78	15.31/15.44	365.84
3	Co(BNHA) ₂ ·4H ₂ O	C ₁₄ H ₂₂ CoN ₄ O ₈	13.60/13.78	38.81/38.61	5.12/4.88	12.93/12.45	433.28
4	Ni(BNHA) ₂ ·3H ₂ O	C ₁₄ H ₂₀ N ₄ NiO ₇	14.14/14.45	40.52/41.08	4.86/4.39	13.50/13.37	415.03
5	Pb(BNHA) ₂	C ₁₄ H ₁₄ N ₄ O ₄ Pb	40.67/40.33	33.00/33.19	2.77/2.57	11.00/10.98	504.49
6	Sn(BNHA) ₂ ·3H ₂ O	C ₁₄ H ₂₀ N ₄ O ₇ Sn	24.99/25.12	35.40/35.59	4.24/3.90	11.29/11.61	475.03
7	La(BNHA) ₃ ·2H ₂ O	C ₂₁ H ₂₅ LaN ₆ O ₈	22.11/22.38	40.11/40.29	4.01/3.33	13.37/12.94	628.37
8	Cr(BNHA) ₃ ·2H ₂ O	C ₂₁ H ₂₅ CrN ₆ O ₈	9.60/9.41	46.58/46.08	4.65/4.21	15.52/15.87	541.46
9	Zn(BNHA)Cl·4H ₂ O ²	C ₇ H ₁₅ ClN ₂ O ₆ Zn	20.18/20.55	25.95/25.36	4.67/4.82	8.65/8.24	324.04

¹M.p. 157°C (dec.) [19]. ²For Cl: 10.94/11.05.

Structure solution and refinement were performed using the SHELX97 program package [22]. Crystal data and details of data collection and structure refinement are given in **Table 2**. Selected bond lengths and angles are listed in **Table 3**.

3. RESULTS AND DISCUSSION

3.1. Electronic Spectra

The electronic absorption spectrum of K(BNHA) (**Figure 1**)

Table 2. Crystal data and details of data collection and structure refinement for Cu(BNHA)₂.

Empirical formula	C ₁₄ H ₁₄ CuN ₄ O ₄
Formula weight	365.83
Temperature (K)	296 (2)
Radiation, λ (Å)	MoK α , 0.71073
Crystal system, space group	Monoclinic, P2 ₁ /n
<i>a</i> (Å)	11.521 (2)
<i>b</i> (Å)	4.6883 (8)
<i>c</i> (Å)	28.979 (5)
β (°)	100.486 (3)
Volume (Å ³)	1539.0 (5)
Z	4
D _{calc} (Mg/m ³)	1.579
F(000)	748
Crystal size (mm)	0.64 ^a 0.03 ^b 0.02
Absorption coefficient (mm ⁻¹)	1.445
Theta range for data collection (deg)	2.54 – 28.46
Limiting indices	-15 ≤ <i>h</i> ≤ 15, -6 ≤ <i>k</i> ≤ 6, -37 ≤ <i>l</i> ≤ 38
Reflections collected /unique [R _{int}]	15423/3892 [0.0461]
Completeness to $\theta = 28.46$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6487
Refinement method	Full-matrix least-squares on F ²
Data/ restraints/parameters	3892/0/208
Goodness-of-fit on F ²	1.024
Final R indices [I > 2 σ (I)]	R1 = 0.0432, wR2 = 0.0922
R indices (all data)	R1 = 0.0831, wR2 = 0.1067
Largest diff. peak and hole, e Å ⁻³	0.424 and -0.247

Table 3. Selected bond lengths *d* (Å) and angles ω (°) in Cu(BNHA)₂.

Bond, angle	<i>d</i> , ω	Bond, angle	<i>d</i> , ω
Cu(1)-O(1)	1.9138 (18)	Cu(1)-O(3)	1.896 (2)
Cu(1)-O(2)	1.921 (2)	Cu(1)-O(4)	1.905 (2)
Cu(1)-N(2) ^a	3.306 (2)	Cu(1)-N(4) ^b	3.118 (3)
O(1)-N(1)	1.319 (3)	O(3)-N(3)	1.312 (3)
O(2)-N(2)	1.306 (3)	O(4)-N(4)	1.320 (3)
N(1)-N(2)	1.275 (3)	N(3)-N(4)	1.274 (3)
N(1)-C(7)	1.469 (3)	N(3)-C(14)	1.476 (3)
O(1)Cu(1)O(2)	82.30 (8)	O(3)Cu(1)O(4)	82.59 (9)
N(2) ^a Cu(1)N(4) ^b	177.87 (6)		
N(1)O(1)Cu(1)	107.49 (15)	N(3)O(3)Cu(1)	107.83 (15)
N(2)O(2)Cu(1)	113.29 (16)	N(4)O(4)Cu(1)	112.72 (16)
O(1)N(1)N(2)	123.9 (2)	O(3)N(3)N(4)	123.5 (2)
N(1)N(2)O(2)	113.0 (2)	N(3)N(4)O(4)	112.6 (2)

^a*x*, *y* + 1, *z*; ^b*x*, *y* - 1, *z*.

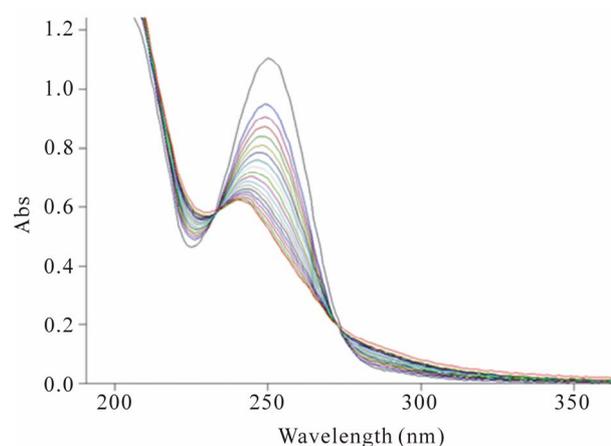


Figure 1. Spectrophotometric titration of an aqueous solution of K(BNHA) (10⁻⁴ M) by the solution of CuCl₂ (10⁻² M).

is characterized by one wide absorption band in the range 230 nm - 260 nm with the λ_{max} 252 nm (log ϵ 4.06).

The addition of metal salts to the solutions of K(BNHA) provokes the hypsochromic shift and decrease in intensity of the ligand absorption band which indicates the change of the electronic structures of the organic anions due to their complexation and formation of coordinate bonds of a co-valent character. $\Delta\lambda_{\text{max}}$ 1 - 19 nm. The presence of isobestic points in the spectra indicates the reversible equilibria in the “ligand-complex” systems. The metal-to-ligand ratio and formation constants of the complexes in aqueous solutions are presented in the **Table 4**.

As the K-BNHA bonds may be considered to be of

Table 4. Composition (ML_n) and stability constants (β) of some metal complexes of BNHA in aqueous solutions and their absorption maxima (λ_{\max} , nm).

Metal ion	n	β	λ_{\max} , nm ($\log \epsilon$)
Mn ²⁺	2	6.82×10^{11}	249 (3.87)
Co ²⁺	2	2.67×10^{10}	245 (3.84)
Ni ²⁺	2	7.51×10^9	245 (3.73)
Cu ²⁺	2	3.43×10^8	238 (3.80)
Zn ²⁺	2	2.3×10^{11}	242 (3.89)
Cd ²⁺	2	4.46×10^{11}	246 (3.96)
Pb ²⁺	2	3.62×10^{10}	248 (3.92)
Ba ²⁺	2	7.45×10^{10}	251 (3.93)
Al ³⁺	3	4.73×10^{14}	233 (3.73)
Cr ³⁺	3	3.22×10^{14}	243 (3.84)
La ³⁺	3	1.28×10^{17}	245 (3.94)
Sm ³⁺	3	1.03×10^{15}	243 (3.89)
Eu ³⁺	3	8.95×10^{15}	242 (3.92)
Er ³⁺	3	1.03×10^{15}	242 (3.92)

100% ionic character, the $\Delta\lambda_{\max}$ value may indicate the increase in the degree of co-valency of M-BNHA interaction. Thus, from the data of the **Table 4** it is evident that among divalent ions of the metals of the 1st transition series, the degree of co-valency of metal-to-ligand interaction changes as following: Mn²⁺ < Co²⁺ = Ni²⁺ < Cu²⁺ > Zn²⁺. The Al-BNHA interactions possess the most covalent character as well as Ba²⁺ forms the coordinate bonds of almost 100% of ionicity.

3.2. IR Spectra

The major IR absorption bands of K(BNHA) and its Cu(II) and Co(II) complexes are presented in the **Table 5**.

The assignments of the various absorption bands in K(BNHA) and the transitional metal complexes were performed according to N. Thakur *et al.* [23] for cupferron and metal cupferrates. It is shown that on complex formation NO stretching frequencies are lowered and the deformation frequencies increased while the C-N and N-N stretching frequencies are not very much altered, indicating that the complex formation takes place through the oxygen of the NO groups.

3.3. Crystal Structure of Cu(BNHA)₂

The copper atom has a nearly planar square coordination formed by oxygen atoms of two BNHA-ligands, which close 5-membered ONNOCu chelate rings (**Figure 2**).

The Cu(1) atom lies in the plane of the O(1)N(1)N(2)O(2) fragment (its deviation is 0.022 Å) and deviates from the O(3)N(3)N(4)O(4) plane by 0.194 Å. In both BGA-molecules, the planar O₂N₂CH₂ and PhCH₂ fragments lie in approximately perpendicular planes (the dihedral angles are 93.3° and 109.9°). The phenyl rings of the two NBHA-molecules are bent in opposite directions with respect to the coordination plane and form an angle of 139.4° with each other. The geometric parameters of the NBHA-ligands in Cu(BNHA)₂ are close to those in Zr(cp)2(BNHA) [24], which is the only compound of NBHA found in the Cambridge Structural Database (version 5.33). Bond lengths (**Table 3**) suggest that π electrons are delocalized over the ONNO chelating groups. The difference between the N-O bond lengths is insignificant, and the N-N bond lengths are close to the double-bond type [25]. This suggests an important contribution of the -O-N+(R)=N-O-canonical form. Cu(BNHA)₂ complexes are packed in stacks running along the b axis (**Figure 3**). In a stack, atoms N(2) and N(4) of neighboring complexes approach the Cu(1) atom by 3.306 (2) and 3.118 (3) Å, respectively, thus completing its coordination to an extremely elongated tetragonal bipyramid.

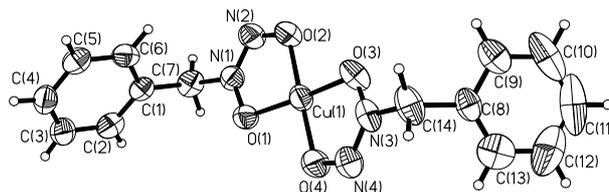


Figure 2. Molecular structure of Cu(BNHA)₂. The thermal ellipsoids are shown at the 50% probability level.

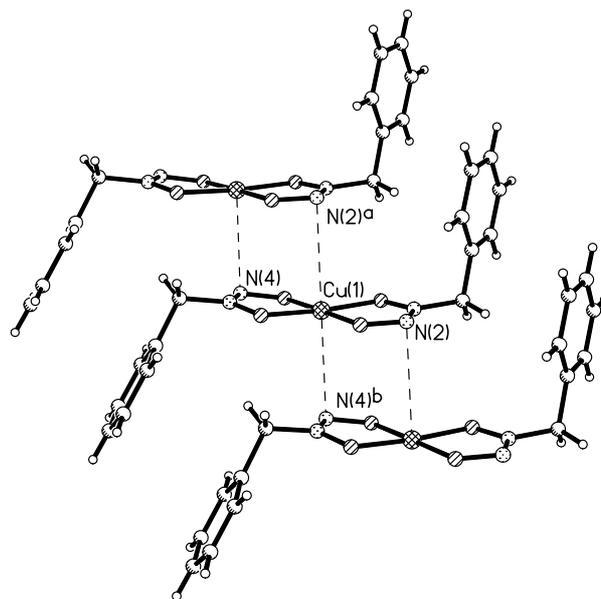


Figure 3. Mutual arrangement of neighboring Cu(BNHA)₂ complexes in a stack.

Table 5. Frequencies (cm^{-1}) and band assignments in K(BNHA) and some transition metal complexes.

K(BNHA)	Cu(BNHA) ₂	Co(BNHA) ₂ ·4H ₂ O	Assignment
3418	3417	3345	C-H stretching vibration
3150	3120	3243	N-H stretching vibration
1650	1633	1646	C=C ring stretching vibration
1434	1417	1425	C-N stretching vibration
1397	1344	1395	NN stretching vibration
1231	1214	1222	NO stretching vibration
1145	1149	1145	C-N ring in-plane vibration
961	940	929	Ring vibration
784	783	783	C-H ring out of plane vibration
705	717	707	C=C ring out of plane vibration

4. CONCLUSION

The N-benzyl-N-nitrosohydroxylamine (BNHA) ligand coordinates metal ions by two oxygen atoms. The bonding of the ligands to metal ions is confirmed by spectroscopic and single-crystal X-ray diffraction studies. The composition and the formation constants of the complexes in aqueous solutions were determined by UV spectroscopic titration.

5. SUPPLEMENTARY MATERIAL

The crystallographic data for Cu(BNHA)₂ have been deposited with the Cambridge Crystallographic Data Centre (CCDC 910807).

6. ACKNOWLEDGEMENTS

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