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Synthesis of a new five-coordinate ternary copper (II) complex: crystal structure and spectral studies

A.R. Rezvani[1], H. Janani[1], F. Rostami-Charati[2*], B.W. Skelton[3]

[1]Department of Chemistry, University of Sistan and Baluchestan, PO Box 98135-674, Zahedan, Iran,
[2]Department of Chemistry, Faculty of Science, Gonbad Kavous University, P.O. Box 163, Gonbad, Iran
[3]Chemistry, School of Biomedical, Biomolecular & Chemical Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, Perth,Western Australia 6009, Australia

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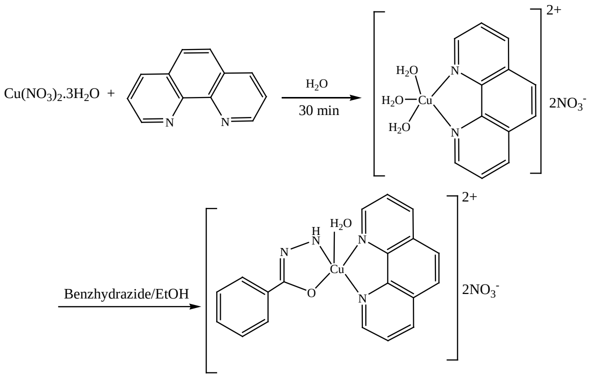
A new ternary complex of benzhydrazide-phenanthroline-H_2O ligands with copper (II) was synthesized and characterized by elemental analysis, infrared spectroscopy and UV-Vis electronic absorption spectroscopy. The crystal and molecular structure of $[Cu(BH)(Phen)(H_2O)\ ]_2NO_3.1.5\ H_2O$ was determined by the single crystal diffraction method which confirmed that the complex has square pyramidal geometry and contains a bidentate heterocyclic ligand on one side and a bidentate benzhydrazide (BH) ligand on the other side. This coordination takes place through the nitrogen and oxygen atoms from benzhydrazide and two nitrogen atoms from 1,10-phenanthroline. The apical position is occupied by an oxygen atom from a water molecule as a third ligand.

Keywords: Copper (II) complex, Mixed ligand, X-ray crystal structure, Square pyramidal.

INTRODUCTION

Investigation on mixed ligand systems reveals that ternary complexes are often more stable than expected from statistical reasons [1-3]. They are known for their high stability, and are multifunctional in many fields of chemistry. The mixed chelate complexes of Cu(II) have general formulas such as $[Cu(NN)(NO)]^+$ and $[Cu(NN)(OO)]^+$ that are extremely stable. In addition, they attracted the attention of the scientific community because of their peculiar spectroscopic, photochemical and electrochemical features [4-8]. They also have useful pharmacological benefits. In this set of formulas, two nitrogen atoms (*N,N*) from the phenanthroline molecule represent a di-imine ligand [9]. Herein, we report the synthesis, structure and spectral properties of $[Cu(phen)(BH)(H_2O)]_2NO_3.1.5\ H_2O$ (Scheme 1).



Scheme 1. Synthesis of $Cu(phen)(BH)(H_2O)]_2NO_3$. $1.5H_2O$.

EXPERIMENTAL

Material and methods

All chemicals used were of reagent grade and used without any purification. The IR spectra were recorded in KBr pellets on an FT/IR JASCO 460 spectrophotometer in the range of 4000-400 cm^{-1}. Elemental analysis for C, H and N was performed on a Heraeus CHN-O-Rapid elemental analyzer. Electronic spectral measurements were performed using a JASCO 7850 spectrophotometer.

General procedure for the synthesis of $[Cu(phen)(BH)(H_2O)]_2NO_3.\ 1.5\ H_2O$

Magnetically stirred solution of $Cu(NO_3)_2.3H_2O$ (1 mmol, 0.2416 g) and 1,10-phenanthroline (1mmol, 0.198g) in water (10 mL) immediately produced a blue colored solution. After that, ethanolic solution of benzhydrazide (1 mmol, 0.136 g) was slowly added. Then, the resulting solution was filtered and allowed to evaporate slowly at room temperature. After one week, blue crystals of the complex were formed.

RESULTS AND DISCUSSION

The procedure was simple and easy to handle. The structure of the compound $Cu(phen)(BH)(H_2O)]2NO_3.1.5\ H_2O$ was characterized by single crystal X-ray diffraction. The single crystals of the complex, obtained by slow evaporation from its aqueous ethanolic solution, were suitable for X-ray diffraction study (Figure 1).

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* To whom all correspondence should be sent:
E-mail: f_rostami_ch@yahoo.com

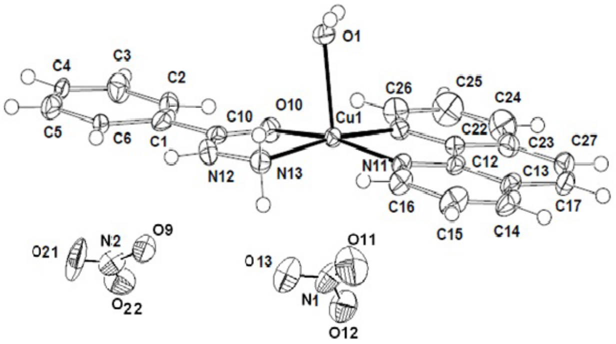

Fig.1 Molecular structure of the complex [Cu(phen)(BH)(H_2O)]2NO_3.1.5 H_2O projected oblique the coordination plane. Only one component of the disordered atoms is shown.

Infrared spectral study

The IR spectrum of the complex displays an absorption band at 1552 cm^{-1} that is related to the C=N moiety of Phen [10]. The basal positions are occupied by the nitrogen atoms of the heterocyclic base that represents the absorption of Cu-N, which is seen in the range of 400-4000 cm^{-1}. This phenomenon is due to the heterocyclic ring [11-12]. Besides, Cu-O vibration was observed at 455 cm^{-1} in the IR spectrum. The spectrum of the water molecule was observed at 3422 cm^{-1} [13]. When this complex was heated for 15-20 min at 100°C, the Cu-O bond did not disappear from the IR spectrum. This observation indicates that the water molecule in this complex is a coordinated ligand with the copper (II) ion. The band observed at 1764 cm^{-1} is related to the nitrate group in the crystal lattice of the complex [14].

Electronic spectrum

The electronic spectrum of the complex in solution was recorded in various solvents (MeOH, EtOH and DMF) and their maximum parameter was approximately the same in all solvents. The spectrum exhibited a d-d transition as a broad band centered at 675 nm. The $\pi \rightarrow \pi^*$ intraligand transitions in the phenyl group were observed in the 220-270 nm region [15,16]. The electronic spectral data of the complex in ethanol solution are listed in Table 1.

Table 1. Electronic absorption solution data [10^{-4} M]

Solution (EtOH) λ_{max} (nm)	Assignments
675	d-d
272	$\pi \rightarrow \pi^*$
224	$\pi \rightarrow \pi^*$

X- ray crystallography

Single crystal structure of the complex was established from X-ray diffraction. The extracted crystal data of the complex are summarized in Table 2 and the structure of the complex is depicted in Fig. 1. Herein, by considering the structure of X-rays, we could explain that ellipsoid atoms have been drawn at the 50% probability level. Selected coordination geometries are shown in Table 3.

Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini diffractometer fitted with graphite-monochromated Mo Kα radiation yielding N_{total} reflections, these merging to N unique after analytical absorption correction (R_{int} cited), with N_o reflections having $I > 2\sigma(I)$. The structure was refined against F^2 with full-matrix least-squares using the program SHELXL-97 [17]. The phenyl ring of the benzohydrazine ligand is disordered over two sites with equal occupancies. Anions were modeled as being NO_3^- on the basis of refinement. Two of these, NO_3 (2) and NO_3 (3), were disordered about crystallographic inversion centres. Two solvent water molecules, O (2) and O (3), were located with site occupancies for O (3) fixed at 0.5 after trial refinement. Hydrogen atoms of water molecule for O (1) and O (2) were included at located positions and refined with restrained geometries. Those for O (3) were not located. All remaining H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms.

Structural description

The formula of the new synthesized complex is shown in Figs. 1 and 2. The copper is five-coordinate square pyramidal with the apical bond, Cu-H_2O 2.1733(16) Å, longer than those in the basal plane which lie in the range 1.9572(16)- 2.013(2) Å. The hydrazine H atoms are all involved in H-bonding with the oxygen atom from nitrate group. The hydrogen atoms of the dd water molecule form hydrogen bonds with the oxygen atom of nitrate groups and water molecules as solvent O (2), that lead to the formation of a three-dimensional network. The geometrical details are shown in Table 4.

Table 2. Crystal data and structure refinement for the complex

Empirical formula	$C_{19}H_{21}CuN_6O_{9.50}$
Formula weight	548.96
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.0342(9) Å
	b = 9.6415(5) Å
	c = 13.8100(9) Å
	α= 88.668(5)°
	β= 73.969(7)°
	γ = 78.467(6)°
Volume	1132.12(15) $Å^3$
Z	2
Density (calculated)	1.610 Mg/m^3
Absorption coefficient	1.031 mm^{-1}
F(000)	564
Crystal size	0.50 × 0.43 × 0.15 mm^3
θ range for data collection	3.69 to 34.89°
Index ranges	-14<=h<=12, -13<=k<=14, -22<=l<=21
Reflections collected, N_{total}	15814
Independent reflections, N	9095 [R(int) = 0.0255]
N_o, $[I>2\sigma(I)]$	6287
Completeness to θ = 33.50°	99.2 %
Absorption correction	Analytical
Max/min. transmission	0.89/0.66
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9095 / 281 / 407
Goodness-of-fit on F^2	1.019
Final R indices $[I>2\sigma(I)]$	R_1 = 0.0654, wR_2 = 0.1902
R indices (all data)	R_1 = 0.0912, wR_2 = 0.2001
Largest diff. peak and hole	2.601 and -1.574 e.$Å^{-3}$

Table 3. Selected bond lengths [Å] and angles [°] for the complex

Cu(1)-O(10)	1.9572(16)
Cu(1)-N(21)	1.9813(18)
Cu(1)-N(11)	2.0047(18)
Cu(1)-N(13)	2.013(2)
Cu(1)-O(1)	2.1733(16)
O(10)-Cu(1)-N(21)	92.20(7)
O(10)-Cu(1)-N(11)	167.24(7)
N(21)-Cu(1)-N(11)	82.86(7)
O(10)-Cu(1)-N(13)	82.18(8)
N(21)-Cu(1)-N(13)	168.82(8)
N(11)-Cu(1)-N(13)	100.59(8)
O(10)-Cu(1)-O(1)	92.17(7)
N(21)-Cu(1)-O(1)	98.71(7)
N(11)-Cu(1)-O(1)	100.19(7)
N(13)-Cu(1)-O(1)	91.18(8)
C(16)-N(11)-C(12)	118.23(19)
C(16)-N(11)-Cu(1)	130.03(16)
C(12)-N(11)-Cu(1)	111.71(13)
C(10)-O(10)-Cu(1)	113.08(14)
N(12)-N(13)-Cu(1)	106.68(14)

Table 4. Hydrogen bonds for g 44 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(12)-H(12)...O(31)^{2}	0.88	1.72	2.566(8)	159.5
N(12)-H(12)...O(32)	0.88	2.02	2.886(9)	169.8
N(13)-H(13A)...O(23)	0.92	2.07	2.929(4)	154.8
N(13)-H(13A)...O(22)^{1}	0.92	2.16	2.876(5)	134.5
N(13)-H(13B)...O(11)	0.92	2.16	3.060(3)	167.4
O(1)-H(1BO)...O(13)	0.818(15)	1.918(15)	2.728(3)	171(3)
O(1)-H(1AO)...O(2)	0.791(13)	1.933(14)	2.720(3)	173(4)
O(2)-H(2AO)...O(3)	0.903(17)	2.26(2)	2.827(5)	120(2)
O(2)-H(2BO)...O(13)^{3}	0.840(16)	1.984(19)	2.783(3)	159(3)

Symmetry transformations used to generate equivalent atoms:
^{1} -x,-y,-z+1; ^{2} -x+1,-y,-z+1; ^{3} -x+1,-y+1,-z

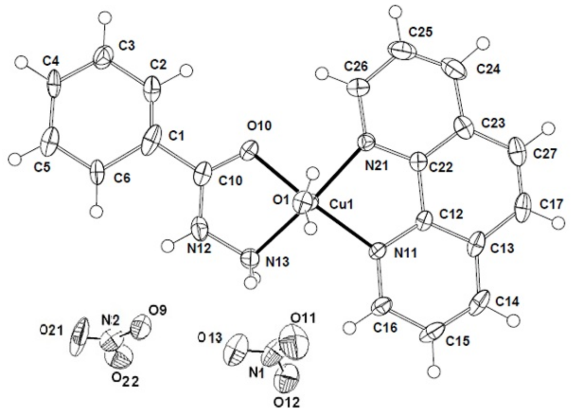

Fig. 2. Molecular structure of the complex projected onto the coordination plane. Only one component of the disordered atoms is shown.

CONCLUSION

The present paper reports the synthesis, characterization and crystal structure of a new five-coordinate ternary copper (II) complex. In the structure of the complex the copper atom has square pyramidal coordination geometry. This coordination is due to two nitrogen atoms from phenyl groups of phenanthroline and one oxygen and one nitrogen atoms from benzhydrazide in the basal plan. The water molecule occupies the axial position. Unique properties are observed for Cu^{2+} complexes containing an aromatic diimine and bidentate ligand with oxygen and nitrogen atoms [18-20]. The effective magnetic moment (μeff) of the complex was measured by the Evans method. The magnetic moment of the complex in crystalline state at 300K was found to be 1.92 B.M which is consistent with the spin only values for mononuclear d9 copper (II) system [21-23]. The elemental analysis data are consistent with a 1:1:1 ratio of the metal ion: benzhydrazide: heterocyclic base for the synthesized complex.

Crystal data of [Cu(phen)(BH)(H_2O)]2NO_3. 1.5 H_2O

Crystallographic data (except structure factors) for the structure have been deposited in the Cambridge Crystallographic Data Centre as a supplementary publication CCDC 1007750. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Summary of Data CCDC 1007750; Formula: $C_{19}H_{21}CuN_6O_{9.50}$; Unit cell parameters: a 9.0342(9) Å, b 9.6415(5) Å, c 13.8100(9) Å; α= 88.668(5)°, β= 73.969(7)°, γ = 78.467(6)°; space group $P\bar{1}$.

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СИНТЕЗА НА НОВ ТРЕТИЧЕН МЕД (II) КОМПЛЕКС: КРИСТАЛНА СТРУКТУРА И СПЕКТРАЛНИ ИЗСЛЕДВАНИЯ

А. Реза Резвани[1], Х. Джанани[1], Ф. Ростами-Чарати[2*], Б.У. Скелтън[2]

[1,2]Департамент по химия, Университет на Систан и Балучестан, Захедан, Иран
[2]Департамент по химия, Научен факултет,Универсотет „Гонбад Кавус“, Гонбад, Иран
[3]Департамент по химия, Училище за биомедицински, биомолекулни и химически науки, Университет в Западна Австралия, Пърт, Западна Австралия 6009, Австралия

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(Резюме)

Синтезиран е нов третичен комплекс на мед (II) с лиганди от бензхидразид фенантролин- H_2O и е охарактеризиран чрез елементен анализ, инфрачервен спектър и UV-Vis електронен абсорбционен спектър. Определена е кристалната и молекулна структура на $[Cu(BH)(Phen)(H_2O)]_2NO_3.1.5\ H_2O$ по метода на единичната кристална дифракция, което потвърждава, че комплексът има квадратна пирамидална геометрия и съдържа би-дендатен хетероцикъл от едната страна и би-дендатен бензхидразид (BH) от другата страна. Тази координация се осъществява чрез азотния и кислородния атом от бензхидразида и два азотни атома от 1,10-фенантролина. Противоположната позиция се заема от кислороден атом от водната молекула като трети лиганд.