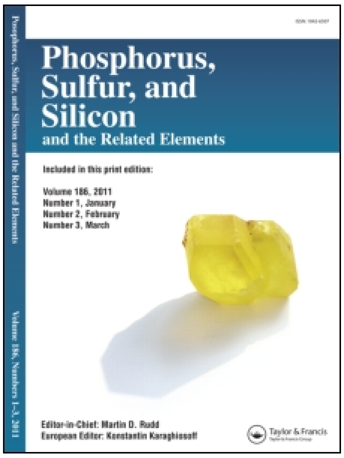

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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF CO(II), NI(II), CU(II) AND ZN(II) WITH 6-SUBSTITUTED-4-ARYL-3-CYANO-PYRIDINE-2(1H)-THIONES

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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF CO(II), NI(II), CU(II) AND ZN(II) WITH 6-SUBSTITUTED-4-ARYL-3-CYANO-PYRIDINE-2-(1H)-THIONES

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Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with 6-substituted 4-aryl-3-cyano-pyridine-2-(1H)-thiones have been prepared and characterized by elemental analysis, IR, UV-Visible and ^{1}H-NMR spectroscopy, molar conductivity, magnetic moment measurements and x-ray diffraction analysis. According to magnetic measurements and UV-Visible spectra, nickel(II) and copper(II) complexes are suggested to have square-planar structure whereas cobalt(II) complexes has either tetrehedral or square planar geometries. X-ray diffraction analyses suggested the orthorhombic powder structure unit for Ni(II) and Cu(II) complexes and triclinic for Co(II) ones.

Key words: 6-Substituted-4-aryl-3-cyano-pyridine-2-(1H) thiones; pyridine-thione complexes; metal ion complexes; spectroscopy; magnetic moments; conductivity.

INTRODUCTION

The biological importance of pyridine-2-thiones has resulted in great interest in their synthesis and chemistry.[1–3] In previous work,[4–7] we have reported a variety of novel procedures for the synthesis of 3-cyanopyridine-2-(1H)-thiones and conversion of these compounds into thieno[2,3-b] pyridines of biological interest. As a logical extension of this work, we have reported in the present paper, the chelating behaviour of 6-substituted-4-aryl-3-cyano-pyridine-2-(1H)-thiones towards Co(II), Ni(II), Cu(II) and Zn(II) ions.

EXPERIMENTAL

Materials

All organic materials and the metal salts used were of reagent grade (BDH or Merck products). 6-Substituted-4-aryl-3-cyano-pyridine-2-(1H)-thiones were prepared according to the method described in our previous work.[7]

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TABLE I

Analytical data, molar conductivity and magnetic moment values of $(NS—R_1R_2)_2M$ complexes

M	R_1	R_2	C % Found (calc.)	H % Found (Calc.)	N % Found (Calc.)	μ_{eff} B.M.	Λ ohm^{-1} cm^2 mol^{-1}	Yield %	M.P.°C
Co	*p*-$CH_3OC_6H_5$	C_6H_5	65.5(65.8)	3.9(3.7)	8.3(8.0)	4.4	12	72	302-4
Ni	*p*-$CH_3OC_6H_4$	C_6H_5	65.7(65.8)	3.8(3.7)	8.4(8.0)	—	8	70	290-2
Cu	*p*-$CH_3OC_6H_4$	C_6H_5	65.6(65.3)	3.6(3.7)	8.5(8.0)	1.73	9	75	302-4 (decp.)
Co	*p*-$CH_3OC_6H_4$	CH_3	59.3(59.0)	3.9(3.8)	10.0(9.8)	4.3	6	69	310
Ni	*p*-$CH_3OC_6H_4$	CH_3	59.5(59.0)	3.7(3.8)	9.6(9.8)	—	8	68	303-5
Cu	*p*-$CH_3OC_6H_4$	CH_3	58.8(58.4)	4.0(3.8)	9.3(9.6)	1.75	10	70	225-27
Co	C_6H_5	C_6H_5	68.1(68.2)	3.6(3.4)	8.7(8.8)	4.6	14	67	290-1 (decp.)
Ni	C_6H_5	C_6H_5	68.4(68.2)	3.2(3.4)	8.5(8.8)	—	15	65	229-231
Cu	C_6H_5	C_6H_5	67.3(67.7)	3.1(3.4)	8.3(8.6)	1.74	7	68	285-7
Co	C_6H_5	CH_3	61.6(61.3)	3.7(3.5)	11.2(11.0)	4.7	9	63	310
Ni	C_6H_5	CH_3	61.8(61.3)	3.6(3.5)	11.4(11.0)	—	11	64	302-1
Cu	C_6H_5	CH_3	60.9(60.7)	3.3(3.5)	11.0(10.8)	1.72	13	66	289-3
Co	*p*-ClC_6H_4	C_6H_5	61.8(61.5)	2.9(2.8)	8.0(7.8)	4.7	5	58	310
Ni	*p*-ClC_6H_4	C_6H_5	61.4(61.5)	3.0(2.8)	8.1(7.8)	—	8	59	310
Cu	*p*-ClC_6H_4	C_6H_5	61.3(61.1)	2.6(2.8)	7.9(7.8)	1.73	10	60	309-10 (decp.)
Co	*p*-ClC_6H_4	CH_3	53.5(53.9)	2.6(2.7)	9.5(9.6)	4.3	6	55	310
Ni	*p*-ClC_6H_4	CH_3	54.4(54.0)	2.8(2.7)	9.4(9.6)	—	8	56	302-1
Cu	*p*-ClC_6H_4	CH_3	53.6(53.5)	2.4(2.7)	9.5(9.6)	1.75	5	57	301
Ni	*p*-$N(CH_3)_2$	C_6H_5	66.7(66.7)	4.1(4.4)	11.9(11.6)	—	6	72	295-7
Zn	*p*-$N(CH_3)_2$	C_6H_5	66.5(66.1)	4.3(4.4)	11.2(11.5)	—	4	58	280-3

Preparation of Metal Complexes

The metal complexes were prepared by adding 50 ml ethanolic solution of $Ni(CH_3COO)_2 \cdot 4H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$ or $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.1 mol) to 100 ml of DMF solution of the ligand (6-substituted-4-aryl-3-cyano-pyridine-2-(1H)-thiones) (0.2 mol). The reaction mixture was heated under reflux with continuous magnetic stirring for about one hour. The solution was then reduced to a small volume and left to cool whereby the complexes separated as fine precipitates. These complexes were filtered off, washed with ethanol, dried and preserved in a desiccator over silica gel.

Physical and Spectral Measurements

Elemental analyses were carried out at the microanalysis laboratory, Faculty of Science, Cairo University. The electronic spectra in DMF were recorded using a Spectronic 2000 spectrophotometer. The infrared spectra were measured using KBr discs with a Beckman IR 20 spectrophotometer. The magnetic measurements were carried out by the Gouy method at room temperature. The apparatus was calibrated with mercury tetrathiocyanato cobaltate(II). Diamagnetic corrections were made using Pascal's constants. Conductivity measurements were made at 25°C in DMF using a YSI conductivity bridge Model 31 using a dip cell (cell constant = 1). Proton nuclear magnetic resonance spectra were measured in CD_3SOCD_3 on a Varian EM 390 NMR Spectrophotometer. Chemical shifts are reported in ppm downfield internal trimethylsilane (δ). Jeol x-ray diffractometer model JSX-60PA was used for recording the diffraction patterns. The patterns were run using Cu K_α radiation (λ = 1.54184 Å) and Ni filtered. The scanning speed was 2°/min and chart speed 1 cm/min.

RESULTS AND DISCUSSIONS

Analytical data obtained for the metal complexes under investigation are given in Table I. The data suggest a 1:2 stoichiometry of the general formula ML_2 where L = 6-substituted-4-aryl-3-cyanopyridine-2-(1H)-thione ligands (Figure 1), and M = Co(II), Ni(II), Cu(II), and Zn(II). The very low values of molar conductivities (Table I) determined in *N*,*N*-dimethylformamide, suggest the non-electrolytic nature of these complexes.[8]

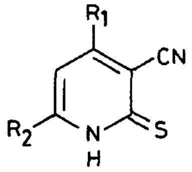

FIGURE 1 Structure of the ligands; $R_1 = C_6H_5$—, p-$CH_3OC_6H_4$, p-$N(CH_3)_2$, p-ClC_6H_4— and $R_2 = CH_3$ or C_6H_5.

Infrared Spectra

The fundamental infrared bands recorded for all the complexes are given in Table II. The very sharp absorption band at 2230 cm^{-1} due to the stretching vibration of the cyano group (CN) in the free ligands is present at the same position in the spectra of all complexes, indicating that the cyano group at position 3 is not involved in the complex formation. Comparison of the infrared spectra of the free ligands with their corresponding metal complexes spectra shows the disappearance of the bands at 1190 and 2980 cm^{-1} attributed to the stretching vibration of C=S and NH groups, respectively with simultaneous appearance of new bands at 760–775 and 1600–1620 cm^{-1} assignable to νC—S and the substituted pyridine respectively. This result indicates the deprotonation of the NH group followed by thioenolization of the C=S group. Furthermore, the far infrared spectra of the metal complexes exhibit new bands in the 445–455 and 370–390 cm^{-1} ranges which may be ascribed to ν(M—N) and ν(M—S), respectively. From the above discussion, it appears that the free ligands are coordinated to the central Co(II), Ni(II), Cu(II) and Zn(II) ions as deprotonated monobasic bidentate ligands through the aromatic tertiary nitrogen atom of pyridine nucleus and the negatively charged sulphur atom forming a four-membered ring as shown in Figure 2. The formation of a four-membered chelating ring is known from similar types of chelates,[9,10] and x-ray crystal structure determinations have shown the presence of 4-membered rings in related systems.[11,12]

TABLE II

The main infrared bands and electronic spectra of (NS—R$_1$R$_2$)$_2$M complexes

M	R$_1$	R$_2$	νC=N cm^{-1}	νC—S cm^{-1}	νM—N cm^{-1}	νM—S cm^{-1}	λ_{max} nm
Co	p-CH$_3$OC$_6$H$_4$	C$_6$H$_5$	1610	770	445	375	600, 290
Ni	p-CH$_3$OC$_6$H$_4$	C$_6$H$_5$	1608	775	445	370	540, 330, 280
Cu	p-CH$_3$OC$_6$H$_4$	C$_6$H$_5$	1600	765	450	380	500, 370
Co	p-CH$_3$OC$_6$H$_4$	CH$_3$	1620	760	455	390	585, 285
Ni	p-CH$_3$OC$_6$H$_4$	CH$_3$	1615	760	450	385	560, 320, 290
Cu	p-CH$_3$OC$_6$H$_4$	CH$_3$	1612	765	448	375	490, 375
Co	C$_6$H$_5$	C$_6$H$_5$	1618	768	445	370	580, 280
Ni	C$_6$H$_5$	C$_6$H$_5$	1600	770	450	370	500, 350, 300
Cu	C$_6$H$_5$	C$_6$H$_5$	1620	770	445	378	510, 360
Co	C$_6$H$_5$	CH$_3$	1620	775	455	385	590, 300
Ni	C$_6$H$_5$	CH$_3$	1610	765	450	388	530, 345, 285
Cu	C$_6$H$_5$	CH$_3$	1610	770	450	390	520, 380
Co	p-ClC$_6$H$_4$	C$_6$H$_5$	1615	760	448	376	600, 300
Ni	p-ClC$_6$H$_4$	C$_6$H$_5$	1605	765	449	380	560, 340, 290
Cu	p-ClC$_6$H$_4$	C$_6$H$_5$	1620	768	446	384	510, 385
Co	p-ClC$_6$H$_4$	CH$_3$	1620	769	452	390	595, 290
Ni	p-ClC$_6$H$_4$	CH$_3$	1610	770	455	386	555, 330, 300
Cu	p-ClC$_6$H$_4$	CH$_3$	1615	772	450	378	490, 390
Ni	p-N(CH$_3$)$_2$	C$_6$H$_5$	1622	775	455	390	560, 350, 300
Zn	p-N(CH$_3$)$_2$	C$_6$H$_5$	1620	775	445	370	—

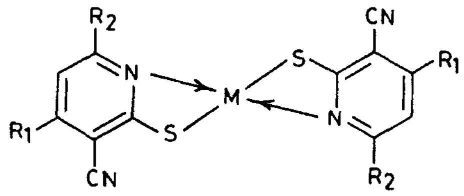

FIGURE 2 Suggested structure of the complexes, abbreviated as $(NS\text{—}R_1R_2)_2M$, M = Co(II), Ni(II), Cu(II) and Zn(II).

Spectral and Magnetic Properties

Copper(II) chelates: The magnetic moment values measured at room temperature for all the complexes are cited in Table I. The magnetic moments observed for copper(II) complexes are found to be in the 1.73–1.78 B.M. range which is close to the spin-only value. The electronic spectra in DMF for all the complexes under investigation are given in Table II. The electronic spectra measured for copper(II) complexes display a broad band at 490–520 nm which probably is due to both d–d transitions[13] $^2A_{1g} \leftarrow {}^2B_{1g}$ and $^2E_{1g} \leftarrow {}^2B_{1g}$. The other band at 360–390 nm can be assigned either to a charge transfer transition or an intraligand electron excitation.[13] The foregoing magnetic and spectral data corresponding to the copper(II) complexes are suggestive of square planar geometry around Cu(II) ion.

Cobalt(II) chelates: The magnetic moments of the cobalt(II) chelates (Table I) varies from 4.3 to 4.7 B.M. and the electronic spectra (Table II) exhibits a broad band at 580–600 nm. The above observations are consistent with either tetrahedral or high spin square planar geometries for the cobalt(II) complexes.[14] The band observed at 280–300 nm may be assigned to a charge transfer transition.

Nickel(II) chelates: Magnetic measurements indicate that all the nickel(II) chelates are diamagnetic. The diamagnetism suggests a four-coordinate square-planar configuration with a singlet ^1Ag ground state. This view may be confirmed by the electronic spectra of these chelates which exhibits three absorption bands at 500–560, 320–350, and 280–300 nm. The band at 500–560 nm has been assigned to the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition which is consistent with the presence of a square-planar nickel(II).[13–16] The higher energy bands are attributed to transitions within the ligands.

Proton Nuclear Magnetic Resonance Spectra

The proton NMR spectra are carried out for the diamagnetic planar nickel(II) complexes investigated in this study. Unfortunately, these complexes dissolved only in dimethyl sulfoxide (DMSO). In this coordinating solvent, the geometrical environment of these complexes changes from diamagnetic square planar to paramagnetic octahedral by accepting two molecules of DMSO in the axial positions. The proton NMR spectrum of the zinc(II) complex of 3-cyano-4-(*p*-NMe_2-phenyl)-6-phenyl-(1H)-2-pyridine thione in deuterated DMSO is shown in Figure 3. The spectrum can be divided into four distinct regions corresponding to resonances resulting from the methyl protons of the *N*-dimethyl group, the phenyl proton

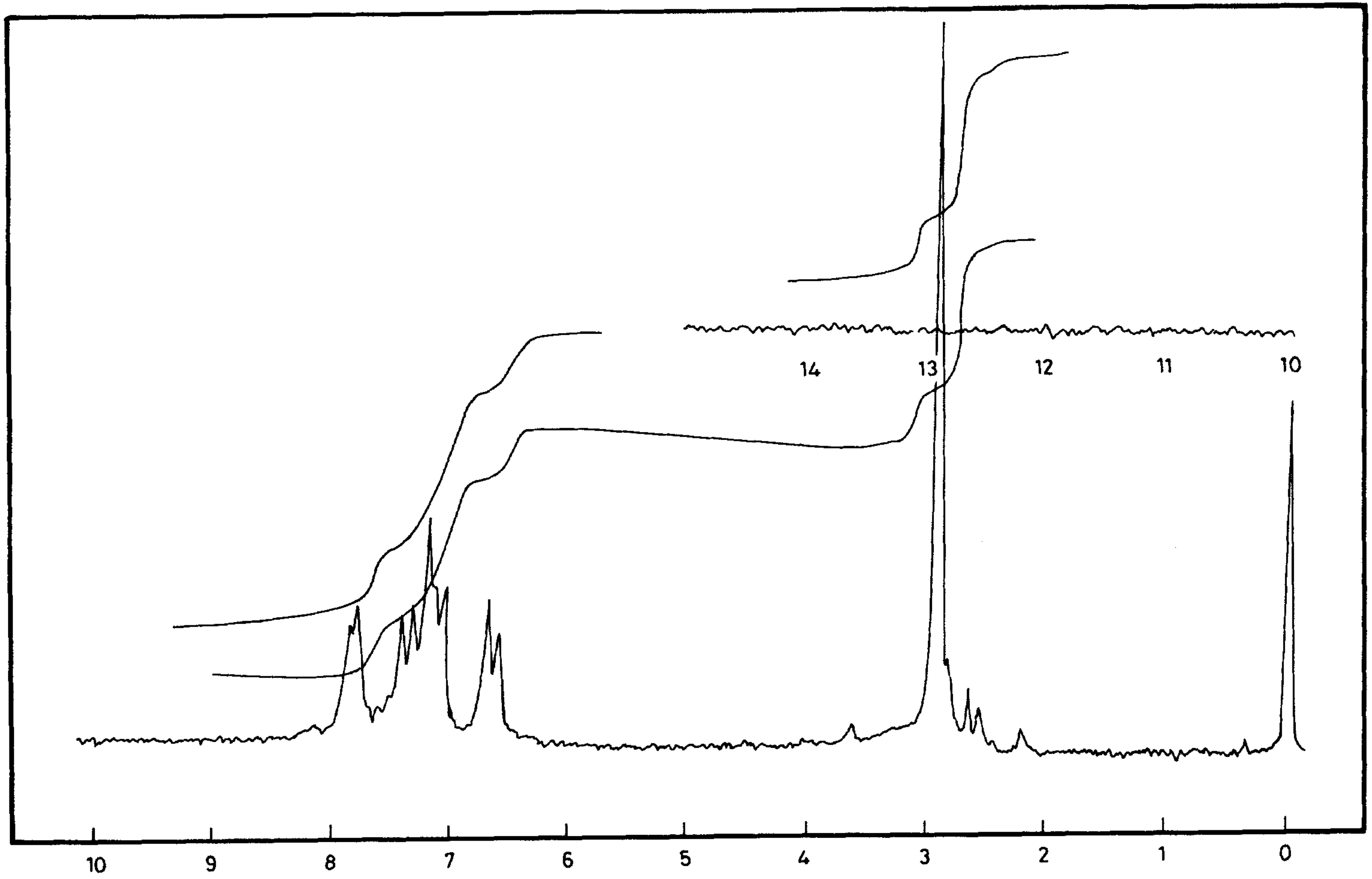

FIGURE 3 Proton NMR spectrum of Zn(II) complexes of 3-cyano-4(p-NMe$_2$ phenyl)-6-phenyl pyridine-2(1H)thione.

(position 6), the aryl protons (position 4) and the aromatic proton of pyridine thione nucleus (position 5). The proton NMR spectrum of this complex reveals a singlet at about 2.85 ppm which was assigned to the methyl groups of the NMe_2 substituent. The spectra also shows a doublet and multiplet in the ranges of 6.55–6.72 and 7.05–7.40 ppm which were assigned to the protons of the aryl moiety (position 4) and the protons of the phenyl (position 6), respectively. The spectra exhibits a singlet at 7.73 ppm which was assigned to the aromatic proton of the pyridine thione nucleus (position 5). Integration of the above proton NMR signals yielded proton ratios of 6:4:5:1, respectively, which is consistent with the above assignment.

The proton NMR spectra of the 3-cyano-4-(p-NMe_2-phenyl)-6-phenyl-(1H)-2-pyridine thione free ligand (Figure 4) exhibited similar features to that observed for its zinc(II) complex (Figure 3) with the exception that the free ligand spectra showed a new peak at about 11.5 ppm. This peak was assigned to the NH proton of the pyridine thione ring. The appearance of NH peak in the proton NMR spectra of the free ligand and the absence of this peak in the spectra of its Zn(II) complex is an indication of the deprotonation of the NH proton of the pyridine thione nucleus upon complexation. Accordingly, the ligand acts as a monobasic bidentate ligand via the nitrogen and thiol sulfur chelating atoms. Such behaviour has been recently reported for the formation of metal complexes of closely structurally related pyrimidine-2-thione ligand.[17] In these complexes, the thiolate anion of pyrimidine-2-thione exhibits S,N-ligation through the ring nitrogen and exocyclic sulfur atoms producing a four-member chelate ring. In the present work, the com-

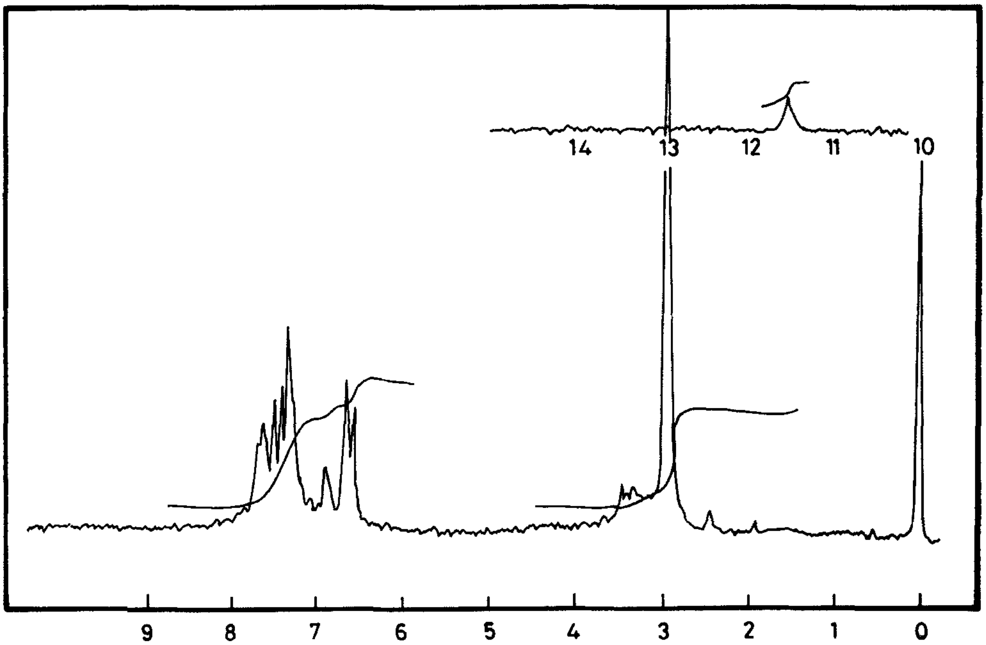

FIGURE 4 Proton NMR spectrum of 3-cyano-4(p-NMe_2 phenyl)-6-phenyl pyridine-2(1H) thione free ligand.

bination of the results of infrared, proton nuclear magnetic resonance spectra, conductivity measurements and elemental analytical data are conclusive evidence that the pyridine-2-thione ligands coordinate via *S*,*N*-ligating atoms in the thiolate anion form.

X-Ray Diffraction Patterns

Ito's method was used to index the powder x-ray diffraction patterns.[14,15] It was found that the powder structure unit of both nickel(II) and copper(II) complexes of 3-cyano-4-(*p*-methoxy-phenyl)-6-phenyl-pyridine-2-(1H)-thione belongs to the orthorhombic system with the dimensions of $a = 17.42$, $b = 13.73$, $c = 12.03$ Å and $\alpha = \beta = \gamma = 90°$ for the nickel(II) complex and $a = 15.18$, $b = 13.14$, $c = 12.04$ Å and $\alpha = \beta = \gamma = 90°$ for the copper(II) complex. Cobalt(II) complex of the same ligand was found to have a tricline system with the dimensions of $a = 19.65$, $b = 17.38$, $c = 8.52$ Å and $\alpha = 87.15$, $\beta = 95.00$, $\gamma = 128.75°$.

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