

# Cobalt(II), Nickel(II), and Copper(II) Complexes with Some 5-Aminopyrazole-Containing Azo Compounds

<sup>a</sup>N. M. RAGEH, <sup>a</sup>A. A. MOHAMAD, <sup>b</sup>S. A. IBRAHIM, and <sup>a</sup>Y. H. EBEAD

<sup>a</sup>Department of Chemistry, Faculty of Science, South Valley University, Qena, Egypt

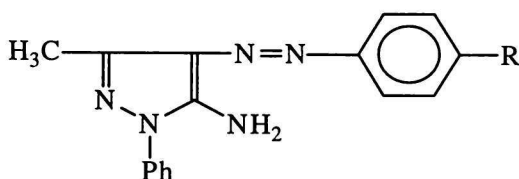
<sup>b</sup>Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt

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The Co(II), Ni(II), and Cu(II) chelates with four heterocyclic azo compounds have been prepared and characterized. Characterization of the solid so obtained was accomplished by elemental and thermogravimetric analysis, electronic and IR spectra, as well as conductivity measurements. The dyes are characterized by high tendency towards complex formation with neutral molecules coordinated to the metal ion as bidentate ligands. The different bands observed in the visible spectra of methanolic solutions of the complexes have been assigned to the possible electronic transition type (L-M CT and  $d-d$ ).

Our interest in the coordination chemistry of biologically active compounds is continued [1–5] to study the ligating properties of some azo phenylpyrazole derivatives. This is because azo compounds are a very important class from the point of view of their interesting structural features [6], reactivity [7], as well as their application as industrial dyes and in biological system where some could be used as inhibitors of tumour growth [6–8].

We report in this paper an investigation of Co(II), Ni(II), and Cu(II) complexes of some azo compounds. The dyes used have the following structure (Scheme 1).



R = H ( $L^1$ ), OCH<sub>3</sub> ( $L^2$ ), COCH<sub>3</sub> ( $L^3$ ), NO<sub>2</sub> ( $L^4$ )

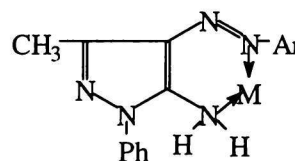
Scheme 1

The molar conductivity values of  $10^{-3}$  mol dm<sup>-3</sup> methanolic solutions of the different complexes synthesized are found to be in the range 20–65 S mol<sup>-1</sup> cm<sup>2</sup>, which indicates a nonelectrolytic nature of these complexes [9]. It should be noted that the relatively high molar conductance values of some complexes are due to the probable solvolysis and dissociation of the complexes in methanol [9].

The chemical analysis data clearly indicate that the neutral molecules and not their monovalent anions

are coordinated to the metal ion. The proposed formula is  $[M(II)L_nCl_2] \cdot xH_2O$ , where  $L = L^1-L^4$ ,  $n = 1$  or 2,  $x = 0-4$  or 6 (cf. Table 1). It is to be noted that some of the known complexes such as  $[M(bipy)_3]Br_2 \cdot 6H_2O$  [10] ( $M = Co(II), Ni(II), Cu(II)$ ) were found to contain a great number of water molecules attached as water of hydration.

Spectrophotometric investigation (in the visible region) of the different complexes was performed to inspect the formation and composition of the most stable complexes possibly formed in solution. The electronic absorption spectra of the ligands ( $L^1-L^4$ ) are characterized by the main visible band in the range 370–434 nm. This band was assigned to an intramolecular CT within the dye molecule [11]. In all cases, this band shows a red shift in the presence of metal ions. This behaviour reveals an instantaneous complex formation between compounds and the metal ion studied, *i.e.* such dyes are characterized by a high tendency towards complex formation. The expected easier intramolecular CT interaction in the complex relative to the free ligand could be ascribed to the highly positive charge of the coordinated metal ion. The intramolecular CT within the complexed ligand can be represented as follows (Scheme 2).



(1  $M^{2+}$  : 1 L) complex

Scheme 2

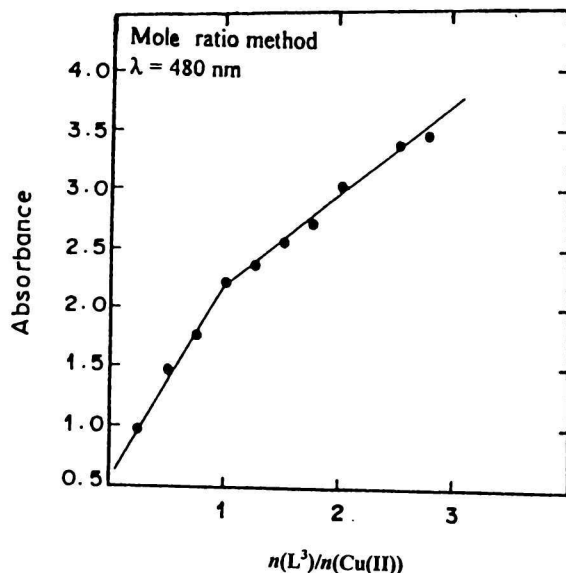
**Table 1.** Elemental Analysis Data, Decomposition Temperatures, and Molar Conductivity Values of the Different Metal Complexes Prepared

	Compound	$\theta/^\circ\text{C}$	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			$\Lambda$ $\text{S mol}^{-1} \text{cm}^2$
			C	H	N	
<i>I</i>	$[\text{CoL}_2^1\text{Cl}_2] \cdot 5\text{H}_2\text{O}$	110	47.34 47.69	4.91 5.01	17.00 17.39	65
<i>II</i>	$[\text{NiL}_2^1\text{Cl}_2] \cdot 6\text{H}_2\text{O}$	105	48.24 48.50	5.31 5.34	17.4 17.6	65
<i>III</i>	$[\text{CoL}^1\text{Cl}_2] \cdot 4\text{H}_2\text{O}$	120	39.90	4.30	14.80	50
<i>IV</i>	$[\text{CoL}_2^2\text{Cl}_2] \cdot 6\text{H}_2\text{O}$	140—142	45.30 45.90	5.40 5.60	15.50 15.76	20
<i>V</i>	$[\text{NiL}^2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	135	44.5 44.31	4.60 4.49	14.90 14.86	55
<i>VI</i>	$[\text{NiL}_2^2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	142	52.15 52.43	5.00 4.92	17.78 17.99	38
<i>VII</i>	$[\text{CuL}^2\text{Cl}_2]$	135	46.42 46.20	3.60 3.80	16.80 15.90	32
<i>VIII</i>	$[\text{CuL}_2^2\text{Cl}_2]$	140	54.33 54.50	4.25 4.50	18.80 18.7	30
<i>IX</i>	$[\text{CoL}_2^3\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	165	52.60 52.56	4.70 4.90	16.90 17.02	48
<i>X</i>	$[\text{CoL}^3\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	180	44.80 44.55	5.28 4.36	14.68 14.40	30
<i>XI</i>	$[\text{NiL}^3\text{Cl}_2] \cdot 4\text{H}_2\text{O}$	170—172	41.25 41.40	4.50 4.80	13.25 13.40	48
<i>XII</i>	$[\text{CuL}^3\text{Cl}_2] \cdot \text{H}_2\text{O}$	139	42.49 42.57	4.40 4.50	14.10 13.80	50
<i>XIII</i>	$[\text{CuL}_2^3\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	125	55.10 54.65	4.55 4.58	17.60 17.70	35
<i>XIV</i>	$[\text{CoL}^4\text{Cl}_2] \cdot 4\text{H}_2\text{O}$	118	37.13 36.66	4.31 4.20	15.90 16.00	52
<i>XV</i>	$[\text{NiL}^4\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	145—147	39.70 39.38	4.00 3.71	17.50 17.22	35
<i>XVI</i>	$[\text{CuL}_2^4\text{Cl}_2]$	155—157	49.50 49.34	3.70 3.62	20.60 21.58	20

The stoichiometric ratio of the Cu(II) ion with  $\text{L}^1$ ,  $\text{L}^3$ , and  $\text{L}^4$  complexes studied was examined by the mole ratio method [12] (all other cases gave unsatisfactory results). The corresponding results are represented graphically in Fig. 1.

Thermogravimetric analysis (TGA) has been performed on a selected number of the prepared complexes with the aim to verify the amount of water molecules that exist in such complexes as well as the way by which they are attached. For example, TGA curve of the  $[\text{CoL}_2^1\text{Cl}_2] \cdot 5\text{H}_2\text{O}$  (*I*) displays two successive mass fraction loss steps. The first one is at a temperature of  $75^\circ\text{C}$  with a mass fraction loss 6.26 %, which corresponds to the loss of three hydration water molecules. The second one occurring at  $165^\circ\text{C}$  corresponds to the mass fraction loss of 4.6 %, which is in accordance with the loss of two crystallization water molecules (*cf.* Fig. 2).

The thermogram of  $[\text{CuL}_2^2\text{Cl}_2]$  (*VIII*) (Fig. 3) shows no mass fraction loss up to  $230^\circ\text{C}$  indicating that this complex does not contain water molecule which confirms the above formula.

**Fig. 1.** The relation between the absorbance and mole ratio  $n(\text{L}^3)/n(\text{Cu(II)})$ .

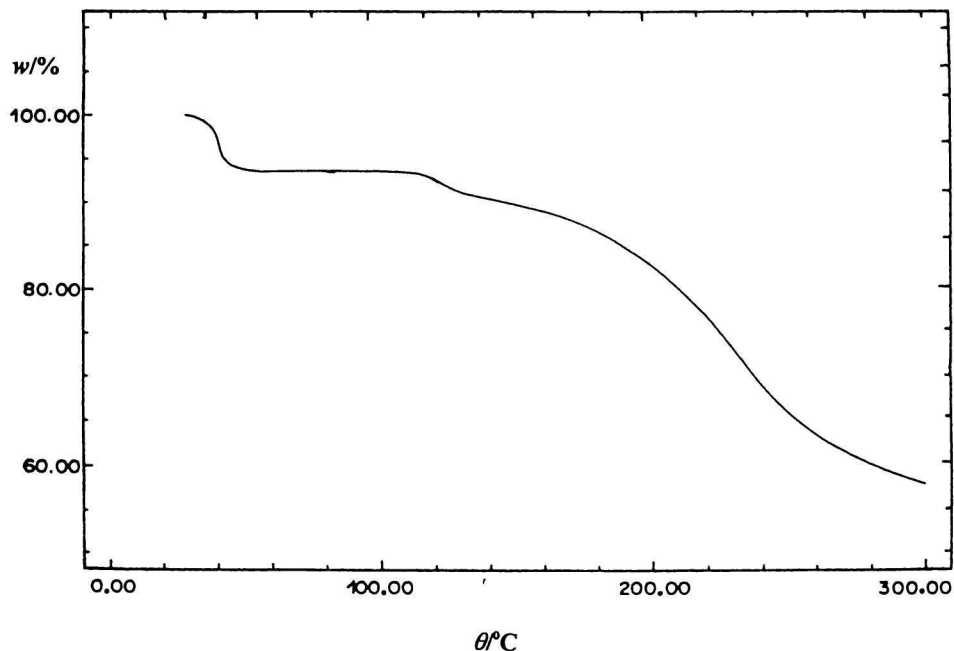


Fig. 2. Thermogram of Co(II)—L<sup>1</sup> complex (compound I).

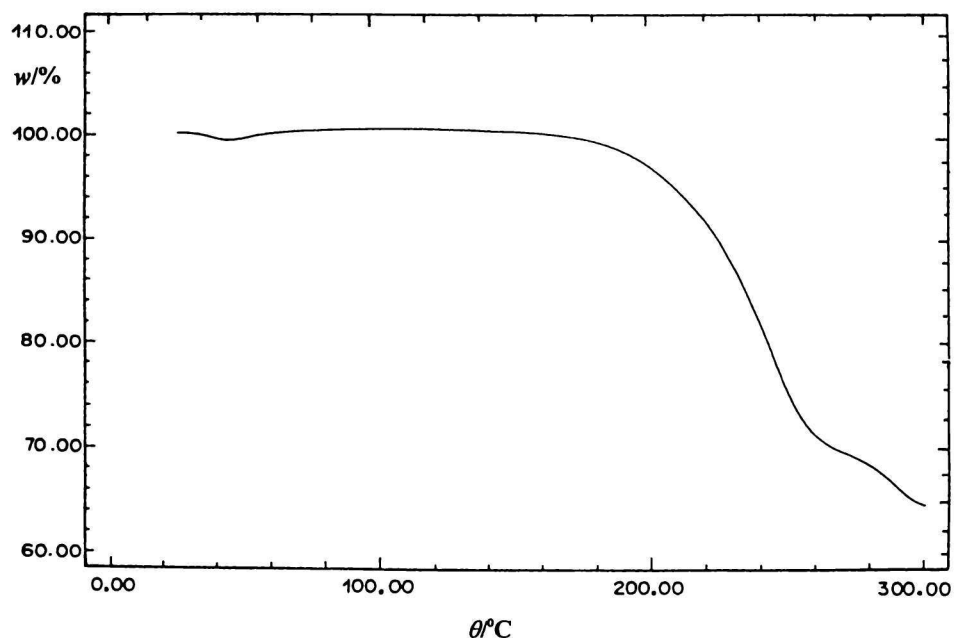


Fig. 3. Thermogram of Cu(II)—L<sup>2</sup> complex (compound VIII).

The electronic absorption spectra of the methanolic solutions of the different complexes have been recorded in the wavelength range 250–600 nm (see *e.g.* Fig. 4). Values of  $\lambda_{\max}/\text{nm}$  and  $\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1}$  are given in Table 2.

The complexes display one or more intense bands in the UV region (below 350 nm) due to intraligand electronic transition (mainly  $\pi-\pi^*$ ). In the visible region the spectra are characterized by an intense band

in the range 367–485 nm. This band is due to CT interaction within the complexed ligand. It is expected that both  $\lambda_{\max}$  and  $\epsilon_{\max}$  of this band acquire some changes upon complexation due to the introduced positively charged metal ion. Such a visible band is usually assigned to charge transfer from ligand to metal (L-M CT), *i.e.* transfer of electrons from orbitals primarily on the metal ion [13].

It is worthy to note here that in case of Cu(II)—L<sup>2</sup>

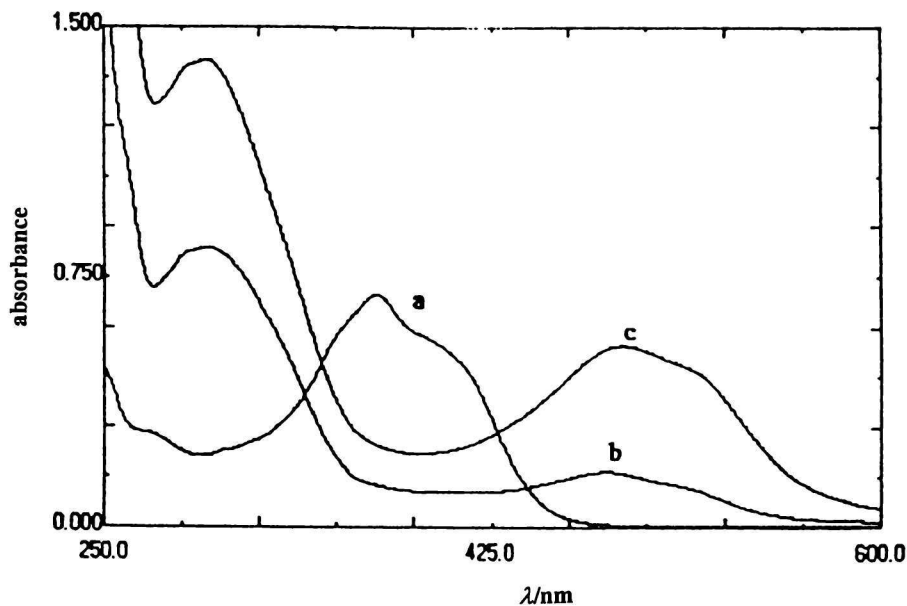


Fig. 4. Electronic absorption spectra of the synthesized complexes. a) Compound V, b) compound VII, c) compound VIII.

Table 2.  $\lambda_{\max}$  and  $\epsilon_{\max}$  of the Characteristic Band of the Methanolic Solutions of the Synthesized M(II)—Ligand Complexes

Compound	$\lambda_{\max}/\text{nm}$	$\epsilon_{\max} \times 10^{-3}/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	Assignment
I	369	39.17	L-M CT
II	372	29.65	L-M CT
III	367	8.20	L-M CT
IV	373	61.25	L-M CT
VI	372	43.00	L-M CT
VII	477	6.55	L-M CT
	296	33.00	$\pi-\pi^*$
VIII	485	13.50	L-M CT
	296	2	$\pi-\pi^*$
IX	398	42.00	
XI	396	24.85	L-M CT
XII	476	5.48	L-M CT
	299	20.77	$\pi-\pi^*$ intra ligand
	262	19.65	$\pi-\pi^*$
XIII	435	18.55	L-M CT
	350	24.70	$\pi-\pi^*$ intra ligand
	308	24.65	$\pi-\pi^*$
XIV	417	13.95	L-M CT
XV	419	13.8	L-M CT
XVI	431	18.7	L-M CT
	315	31.47	$\pi-\pi^*$ intra ligand

complexes (*cf.* Fig. 4), the visible band is accompanied by a broad shoulder at longer wavelengths with  $\lambda_{\max}$  around 515–520 nm ( $19.200\text{--}19.400 \text{ cm}^{-1}$ ). This band appeared as a broad structured one trailing off in the low energy region. It is indicative of a tetragonally distorted octahedral stereochemical configuration of the copper complexes. Since a four-coordination square planar complex is strongly favoured for  $d^9$  configuration, the usual distorted one is that expected by the Jahn–Teller effect. This will result in a transition from  $t_{2g}$  ( $XZ$  or  $YZ$ ) to  $e_g$  ( $X^2-Y^2$ ) [13].

The important bands of infrared spectra of the Co(II), Ni(II), and Cu(II) complexes are recorded in Table 3. The IR spectra of the free ligand display two bands over  $3100 \text{ cm}^{-1}$  due to  $\nu(\text{NH}_2)$ . These bands were found to be completely immersed under strong band due to  $\nu(\text{OH})$  of the water molecules appearing in the  $3225\text{--}3450 \text{ cm}^{-1}$  region. Some complexes display a weak band in the range  $1670\text{--}1703 \text{ cm}^{-1}$  which seems to be an overtone representation. The strong band appearing in the IR spectra of all ligands in the range  $1610\text{--}1640 \text{ cm}^{-1}$ , which is assigned to

**Table 3.** Tentative Assignment of the Important Infrared Bands of the Free Ligands and the Solid Complexes

Compound	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\delta(\text{NH})$	$\nu(-\text{N}=\text{N}-)$	$\nu(\text{Ar}-\text{N}=\text{N}-)$
Free L <sup>1</sup>	330—345	—	1610	1390	1150
I	3350 b	—	1605	1385	weak
II	3330 b	—	1610	1392	1150
Free L <sup>2</sup>	3100—3400	—	1620	1390	1145
V	3350 b	—	1620	1385	1140 w
VI	3400 b	—	1622	1390	1150
VII	—	—	1600	1380	1140
VIII	—	—	1600	1380 w	1150
Free L <sup>3</sup>	3150—3350	1680	1620	1410	1150
IX	3350 b	1680	1620	1415	1160
X	3500	1680	1620	1415	1155
XI	3350	1680	1620	1415	1155
XII	3400 b	1690	1600	1415	1160
XIII	3450 b	1680	1620	1415	1160
Free L <sup>4</sup>	3150—3400	—	1620	1420	1155
XIV	3200 b	—	1610	1415	1160
XV	3250 b	—	1625	1420	1160
XVI	—	—	1600	—	1150

$\delta(\text{NH})$ , was found to locate, in most cases, at lower frequencies in the IR spectra of the resulting metal chelates.

On the other hand, the azo group stretching vibration ( $\nu(\text{N}=\text{N})$ ) appears at lower frequencies in most cases, in the spectra of the complexes relative to its position in the free ligands. In few cases, depending upon the nature of the metal ion this band was found to locate at slightly higher frequencies. These changes indicate the involvement of the azo group in coordination to the metal ion.

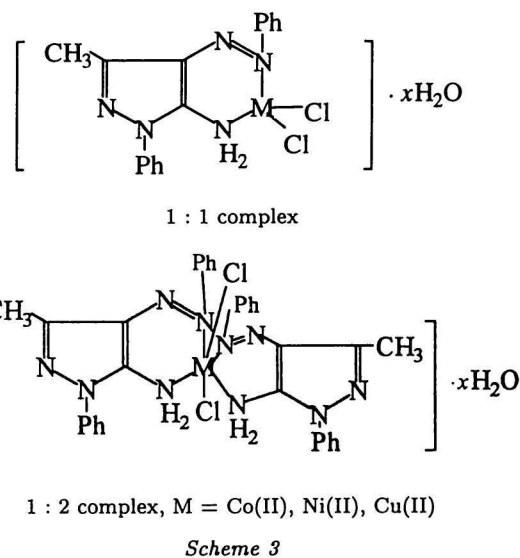
The band appearing in the range 1140—1160  $\text{cm}^{-1}$  in the free ligand can be ascribed to  $\nu(\text{Ar}-\text{N}=\text{N})$ . This band was found to suffer a small shift in the spectra of the complexes. This can be considered as confirmation for the coordination of azo group to the metal ions.

From the foregoing discussion one can conclude that the bonding sites in the present complexes are the azo group and amino group nitrogen atoms. The ligands, therefore, act as neutral bidentate chelating agents. The complexes prepared in this study have the following structures (Scheme 3).

## EXPERIMENTAL

The ligands used in this study have been prepared as described before [14]. 5-Amino-3-methyl-1-phenylpyrazole was prepared according to the procedure previously described [15].

The electronic spectra were recorded on a Shimadzu 2401 PC using 1 cm matched silica cells. The TGA curves were obtained using Shimadzu TGA-50H instrument, the heating rate was 5  $^{\circ}\text{C min}^{-1}$ . The infrared spectra were recorded on Shimadzu 408 spectrophotometer as KBr discs. Conductance measure-



ments were performed using LF Digi-55 conductance bridge using an immersion cell. All measurements were carried out at 25  $^{\circ}\text{C}$ .

## 5-Amino-4-(arylo)-3-methyl-1-phenylpyrazole Derivatives

The appropriate amine (aniline, *p*-anisidine, *p*-acetylaniline or *p*-nitroaniline 0.054 mol) was dissolved in diluted HCl (32  $\text{cm}^3$ ; 5.49 mol) and the resulting solution was cooled in an ice bath to 5  $^{\circ}\text{C}$ . This solution was added dropwise with stirring to a cold solution of sodium nitrite (4 g; 0.058 mol (20  $\text{cm}^3$  of  $\text{H}_2\text{O}$ )).

The resulting diazonium salt was added slowly with stirring to a cold solution (9.3 g; 0.05 mol) of 5-amino-3-methyl-1-phenylpyrazole in 20  $\text{cm}^3$  of diluted HCl. After the completion of the addition, stirring was

continued for 15 min and then a solution of sodium acetate (20 g (60 cm<sup>3</sup> of H<sub>2</sub>O)) was added until complete precipitation of the dye was achieved. The solid precipitate was filtered, washed with cold water, and recrystallized from ethanol to give the corresponding azo derivatives. The purity of these compounds was checked by microanalysis and IR spectroscopy.

### Solid Complexes I—XVI

Complexes were synthesized by mixing hot solutions of both the ligand and metal salts (CuCl<sub>2</sub> · 2H<sub>2</sub>O, CoCl<sub>2</sub> · 6H<sub>2</sub>O or NiCl<sub>2</sub> · 6H<sub>2</sub>O) in the proper ratio ( $w_r = 1:1$  or  $1:2$ ) of the metal to ligand. The mixture was refluxed on water bath for  $\approx 3$  h for copper complexes and 24 h for other complexes and then concentrated by slow evaporation to a small volume and left at room temperature for at least 12 h, whereby the complexes were separated in a microcrystalline form. The solid complexes were filtered, washed several times with cold methanol and kept in a desiccator over P<sub>4</sub>O<sub>10</sub>. The carbon, hydrogen, and nitrogen content of the solid complexes was determined and the analytical data are given in Table 1.

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