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Efficient and convenient template synthesis and characterization of copper(II) and cobalt(II) complexes of 1,1'[arenediylbis(nitrilomethylidine)]bis-2-naphtholes

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Novel Schiff base complexes of Co(II) and Cu(II) derived from 2-hydroxy-1-naphthaldehyde, various diamines and metal (II) acetate via one-pot template and multi-component reactions (MCRs) have been synthesized. The structure of the product was confirmed by several techniques such as elemental analyses (C.H.N), infrared, mass spectroscopy, UV-vis spectra.

Key words: Schiff base complexes, 2-hydroxy-1-naphthaldehyde, multi-component, diamine, synthesis

INTRODUCTION

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. In the area of bioinorganic chemistry interest in Schiff base complexes has centered on the role of such complexes in providing synthetic models for the metal containing sites in metallo-proteins and enzymes [1–5]. Schiff base complexes have been used as drugs and they possess a wide variety of antimicrobial activity against bacteria, fungi, and certain type of tumors [6, 7]. Some drugs increase activity when administered as metal chelates and inhibit the growth of tumors [8, 9]. In the recent years, there has been a considerable interest in the chemistry of transition metal complexes of Schiff bases [10–12]. A large number of reports are available on the chemistry and the biological activities of transition metal complexes containing O, N and S, N donor atoms [13].

Schiff base complexes containing derivatives of salicylaldehyde and aliphatic amines have been studied for their dioxygen uptake and oxidative catalysis because of their similarities to the biological dioxygen carriers, as well as their catalysis properties for the insertion of oxygen into organic substrates. Several metal chelates coordinated through the Schiff base ONNO donors have been studied as oxygen carriers and they are useful models for bioinorganic processes [14–16].

One of the best methods for the preparation of Schiff base complexes is the three-component reactions [17]. The development of multicomponent reactions (MCRs) has emerged as a powerful method in synthetic organic chemistry since they offer one-pot combinations of two or more components in one step, allowing the formation of molecules with more complex structures [18]. These reactions are of increasing importance in the field of medicinal chemistry [19–21].

In continuation of our research on the synthesis of Schiff bases and their complexes of metal ions [22–27], we have studied the preparation of complexes of these Schiff bases with transition metal ions under mild conditions. The corresponding complexes were characterized by spectroscopic and physical data.

RESULTS AND DISCUSSION

In this study, we hope to report the synthesis of Schiff base complexes from 2-hydroxy-1-naphthaldehyde, various diamines and $M(CH_3COO)_2$. The corresponding products were obtained in good to excellent yields and short reaction times in the methanol solution at 50 °C under mild conditions (Scheme 1).

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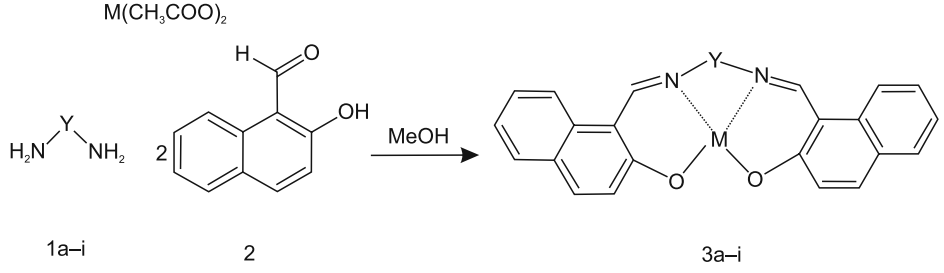
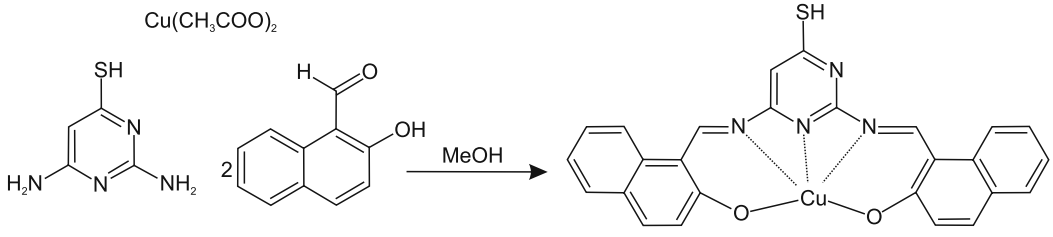
In this study, when 2 mol of 2-hydroxy-1-naphthaldehyde, 1 mol of diamine with 1 mol of $M(CH_3COO)_2$ were allowed to react at 50 °C, the corresponding products were achieved and characterized by spectroscopic and physical data. In this reaction, a lot of useful double Schiff bases were afforded in excellent yields and short reaction times from the one-pot template reaction in the methanol solution and mild condition. The reaction for synthesis of complex **3e** is illustrated in Scheme 2. The results of these reactions are summarized in Tables 1 and 2. As can be seen in these

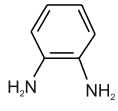
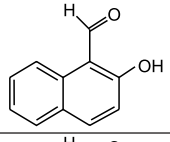
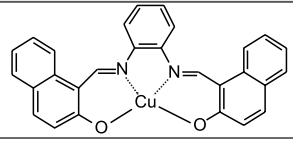
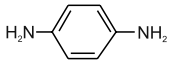
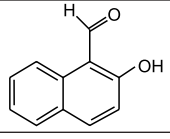
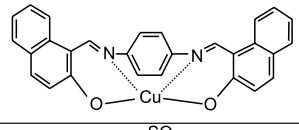
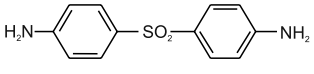
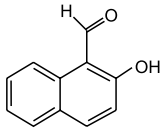
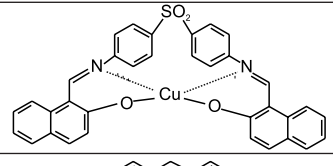
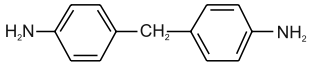
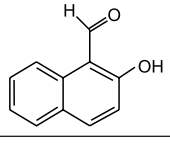
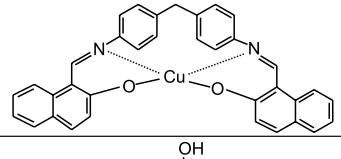
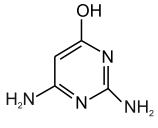
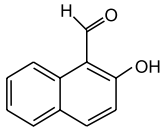
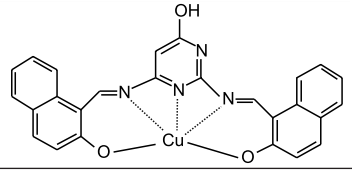
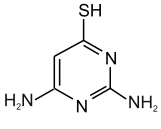
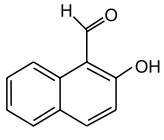
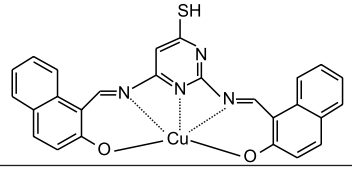


Scheme 1. Synthesis of Schiff base complexes of metal (II)



Scheme 2. Synthesis of compound 3e

Table 1. **The obtained results related to the synthesis of Schiff base complexes of Cu(II)**

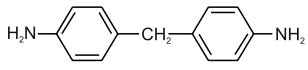
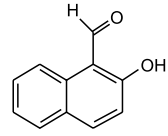
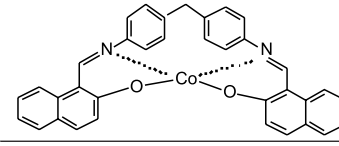
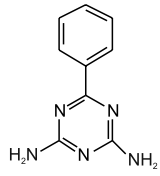
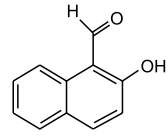
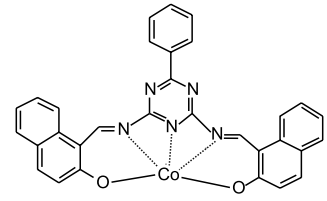
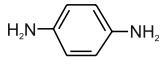
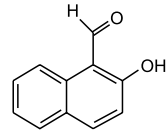
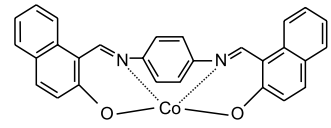
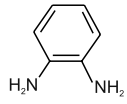
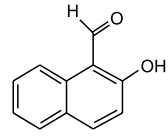
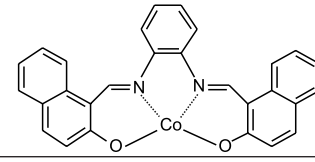
Entry	Diamine	Aldehyde	Product	Time,min	Yield[a], %
1				75	82
2				125	65
3				160	68
4				150	70
5				140	80
6				140	85

[a] Isolated yields based on 2-hydroxy-1-naphthaldehyde.

tables, the corresponding Schiff bases were obtained as a solid, with a melting point between 230–>300. Most of the synthesized complexes are colored and are stable in air, soluble in more organic solvents such as DMSO, DMF, MeOH, EtOH but poorly soluble in diethyl ether.

The structure of products was characterized and confirmed by spectroscopic data. The infrared spectrum of the complexes in comparison with the free ligands was used to determine the changes that might have taken place during the complexation. The band between 1 620–1 650 cm^{-1} is characteristic of the azomethine nitrogen atom in the free ligand. The observed lowering in this frequency to the region 1 600–1 625 cm^{-1} in all the complexes indicates the involvement of the azomethine nitrogen atom (C=N) in coordination with metalation. The spectra of the synthesized ligands show broad bands in the range of 3 100–3 500 cm^{-1} assignable to intramolecular H-bonded phenolic groups, which are absent in the spectra of their complexes, indicating that the oxygen of the –OH groups is coordinated to the metal ion. Thus, the entire ligands act as tetradentate chelating compound coordinated to the metal ion through two oxygen and two nitrogen atoms (Figs. 1 and 2).

Table 2. **The obtained results related to the synthesis of Schiff base complexes of Co(II)**

Entry	Diamine	Aldehyde	Product	Time, min	Yield[b], %
1				160	65
2				145	55
3				130	50
4				120	76

[a] Isolated yields based on 2-hydroxy-1-naphthaldehyde.

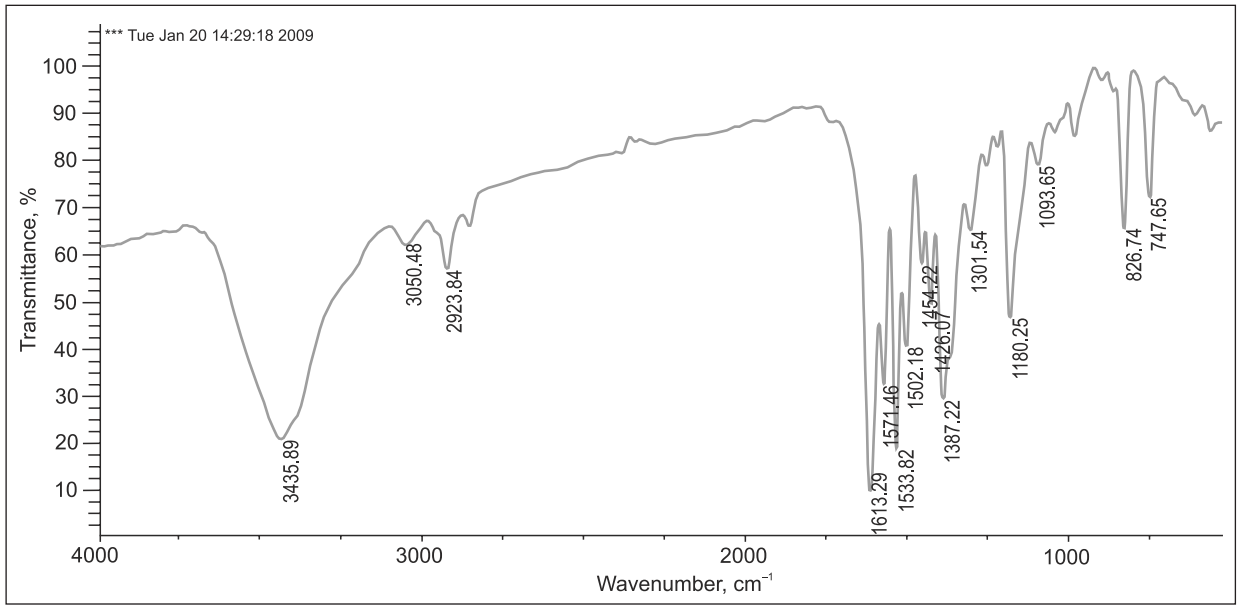


Fig. 1. The IR spectra of 1,1′[4,4′-diphenylmethanebis(nitrilomethylidine)]bis-2-naphthole ligand

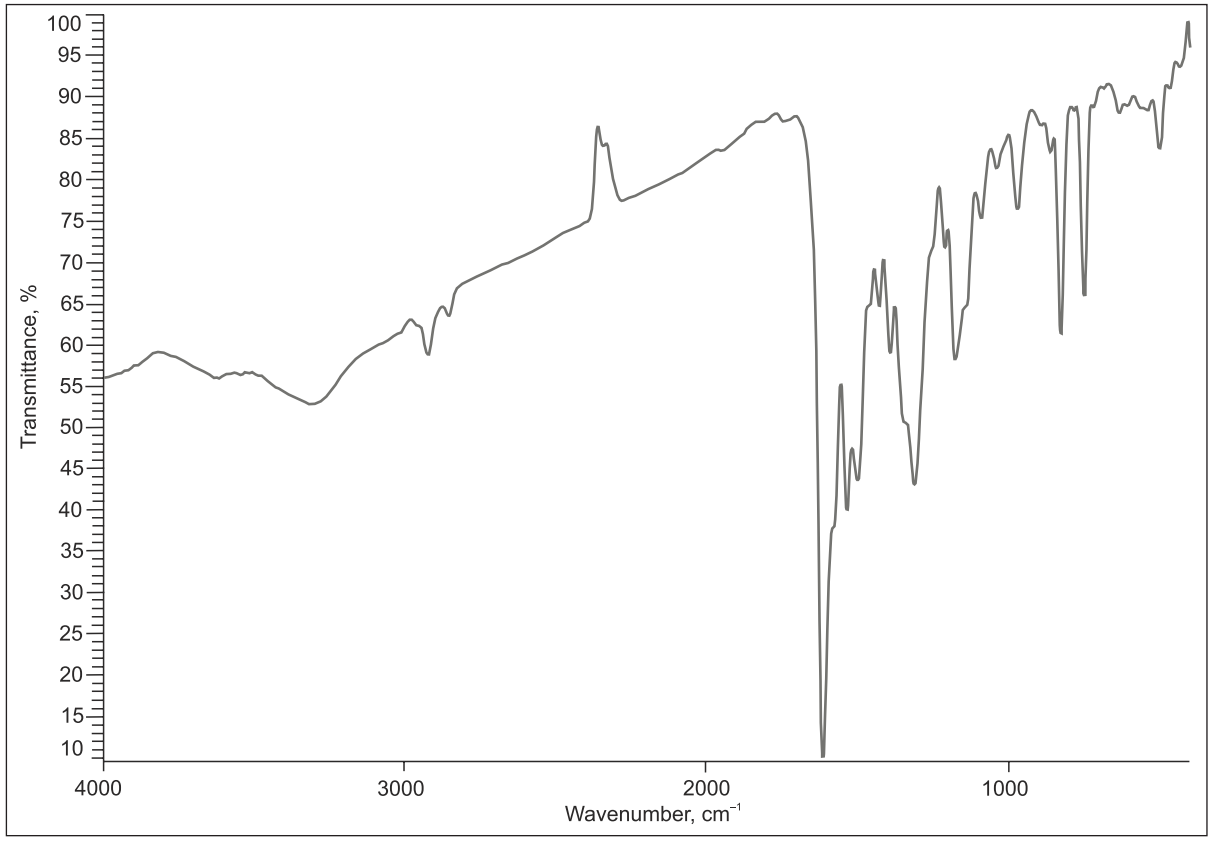


Fig. 2. The IR spectra of complex 1,1'[4,4'-diphenylmethanebis(nitrilomethylidine)]bis-2-naphtholatocobalt (II) (**3h**)

EXPERIMENTAL

Materials

All commercially available reagents were used without further purification and purchased from the Merck Chemical Company in high purity. The amines and naphthaldehyde were purified by standard procedures. Their purity was determined by thin layer chromatography (TLC).

Apparatus

IR spectra were obtained as KBr pellets on a Perkin-Elmer 781 spectrophotometer and on an Impact 400 Nicolet FTIR spectrophotometer. ^{1}H NMR spectra were recorded in DMSO/$CDCl_3$ on a (400 MHz) spectrometer using TMS as an internal reference. Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Mass spectra were recorded on Micro Mass UKLTD spectra by the electron ionization (EI) mode with an ionization voltage of 70 eV. The purity determination of the substrates and reactions monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates.

A typical procedure for the synthesis of Schiff base complexes of Cu(II)

To a mixture of 2,4-diamino-6-hydroxyprimidinethiole (0.14 g, 1 mmol) and $Cu(CH_3COO)_2$ (0.23 g, 1 mmol) in methanol (10 mL) 2-hydroxy-1-naphthaldehyde (0.34 g, 2 mmol) was added by stirring at 50 °C in one portion (Scheme 1). The mixture stirring is continued for 140 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, a solid substance was obtained. The solid product was filtered off and washed with methanol. After drying, the crude product was recrystallized from ethanol to give a pure product. Schiff base complexes were obtained in excellent to good yields and short reaction times. These compounds are identified by physical and spectroscopic data.

1,1'[1,2-Phenylenediylbis(nitrilomethylidine)]bis-2-naphtholatocopper(II) (3a): reddish solid, mp = 231–232 °C; IR (KBr), υ/cm^{-1}: 1 600 (stretch, C=N), 1 403–1 534 (C=C, Ar), 1 162 (stretch, C-O); Anal. calcd. for C. H. N: 71.99 (C), 8.00 (H), 4.54 (N); Found: 71.95 (C), 8.50 (H), 4.53 (N); Mass (m/e): 479 (M^++1, 3), 478 (M^+, 12), 115 (13), 416 (38), 76 (45), 83 (47), 65 (53), 63 (80), 107 (100).

1,1'[1,4-Phenylenediylbis(nitrilomethylidine)]bis-2-naphtholatocopper(II) (3b): brown solid, mp = 249–250 °C, IR (KBr), υ/cm^{-1}: 3 048 (stretch, C-H Aryl), 1 606 (stretch, C=N), 1 501–1 536 (C=C, Ar), 1 176 (stretch, C-O); Anal. calcd. for C. H. N: 70.06 (C), 4.20 (H), 5.84 (N); Found: 69.96 (C), 4.07 (H), 6.15 (N).

1,1'[4,4'-Diphenylmethanebis(nitrilomethylidine)]bis-2-naphtholatocopper(II) (3c): brown solid, mp > 300 °C; IR

(KBr), υ/cm^{-1}: 3 023 (stretch, C-H Aryl), 1 600 (stretch, C=N), 1 502–1 543 (C=C, Ar), 1 182 (stretch, C-O); Anal. calcd. for C. H. N: 74.81 (C), 9.16 (H), 3.64 (N); Found: 74.77 (C), 9.20 (H), 3.61 (N); Mass (m/e): 569 (M^++1, 5), 568 (M^+, 10), 115 (15), 76 (30), 170 (45), 247 (50), 261 (65), 337 (75), 506 (100).

1,1'[4,4'-Diphenylsulfonebis(nitrilomethylidine)]bis-2-naphtholatocopper(II) (3d): brown solid, mp > 300 °C; IR (KBr), υ/cm^{-1}: 3 050 (stretch, C-H Aryl), 1 613 (stretch, C=N), 1 502–1 571 (C=C, Ar), 1 180 (stretch, C-O); Anal. calcd. for C. H. N: 69.07 (C), 9.21 (H), 3.66 (N); Found: 69.11 (C), 99.25 (H), 3.61 (N); Mass (m/e): 620 (M^++1, 5), 619 (M^+, 15), 556 (20), 170 (20), 115 (23), 336 (40), 270 (55), 76 (70), 413 (100).

1,1'[2,6-Pyrimidinediyl-4-thiolbis(nitrilomethylidine)] bis-2-naphtholatocopper(II) (3e): yellow solid, mp > 300 °C; IR (KBr), υ/cm^{-1}: 3 198 (C-H Alkyl), 1 625 (stretch, C=N), 1 464–1 536 (C=C, Ar), 1 292 (stretch, C-O); Mass (m/e): 512 (M^++1, 4), 511 (M^+, 10), 170 (10), 450 (25), 115 (30), 55 (50), 77 (70), 280 (100); Anal. calcd. for C. H. N: 60.75 (C), 3.53 (H), 10.90 (N); Found: 61.11 (C), 3.27 (H), 10.38 (N).

A typical procedure for the synthesis of Schiff base complexes Co(II)

To a solution of 2-hydroxy-1-naphthaldehyde (0.17 g, 2 mmol) and 1,2-phenilendiamine (0.11 g, 1 mmol) in methanol $Co(CH_3COO)_2$ (0.2 g, 1 mmol) was added with stirring at 50 °C in one portion. The stirring was continued to the completion of the reaction. The progress of the reaction was monitored by TLC. After the completion of the reaction, a solid substance was obtained. The solid product was filtered off and washed with methanol. The crude product was purified by recrystallization in ethanol and the pure Schiff base complex was obtained in excellent to good yields after leaving for the appropriate time. The Schiff bases are characterized by physical and spectroscopic data.

1,1'[1,2-Phenylenediylbis(nitrilomethylidine)]bis-2-naphtholatocobalt(II) (3f): yellow solid, mp > 300 °C; IR (KBr), υ/cm^{-1}: 1 600 (stretch, C=N), 1 530 (C=C, Ar), 1 134 (stretch, C-O); Anal. calcd. for C. H. N: 72.29 (C), 8.36 (H), 4.56 (N); Found: 72.32 (C), 8.34 (H), 4.53 (N).

1,1'[1,4-Phenylenediylbis(nitrilomethylidine)]bis-2-naphtholatocobalt(II) (3g): brown solid, mp > 300 °C, IR (KBr), υ/cm^{-1}: 3 025 (weak C-H Alkyl), 1 611 (stretch, C=N), 1 502–1 576 (C=C, Ar), 1 183 (stretch, C-O); Anal. calcd. for C. H. N: 72.59 (C), 9.44 (H), 4.23 (N); Found: 72.55 (C), 9.47 (H), 4.18 (N).

1,1'[4,4'-Diphenylmethanebis(nitrilomethylidine)]bis-2-naphtholatocobalt(II) (3h): brown solid, mp > 300 °C; IR (KBr), υ/cm^{-1}: 3 049 (weak C-H Aryl), 1 618 (stretch, C=N), 1 490–1 541 (C=C, Ar), 1 166 (stretch, C-O); Mass (m/e): 620 (M^++1, 5), 619 (M^+, 15), 556 (20), 170 (20), 115 (23), 336 (40), 270 (55), 76 (70), 413 (100); Anal. calcd. for C. H. N: 75.26 (C), 9.21 (H), 3.66 (N); Found: 75.21 (C), 9.17 (H), 4.1 (N).

1,1'[4-Phenyl-2,6-diyl-1,3,5-triazinebis(nitrilomethylidine)]bis-2-naphtholatocobalt(II) (3i): yellow solid, mp > 300 °C; IR (KBr), υ/cm^{-1}: 1 605 (stretch, C=N), 1 415–1 534 (C=C, Ar), 1 186 (stretch, C-O); Mass (m/e): 553 (M^++1, 7), 552 (M^+, 15), 495 (20), 115 (25), 78 (37), 182 (50), 77 (85), 155 (100).

CONCLUSIONS

In the present wok, we have reported a mild, easy, clean and an efficient method for the synthesis of some novel Schiff base complexes of metal (II) under mild conditions at 50 °C. Also the desired Schiff bases for the preparation of these complexes have been obtained through easy, simple, three component reaction of 2-hydroxy-1-naphthaldehide with various diamines and metal (II) acetate in methanol solution. The crude products were purified by recrystallization in ethanol and the pure Schiff base complex was obtained in excellent yields and with short reaction times.

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EFEKTYVI IR PATOGI ŠABLONINĖ VARIO (II) IR KOBALTO (II) KOMPLEKSŲ SU 1,1'[ARENODIILBIS(NITRILOMETILIDINO)] BIS-2-NAFTOLAIS SINTEZĖ IR JŲ APIBŪDINIMAS

S a n t r a u k a

Aprašyta naujų Šifo bazių kompleksų paprasta ir patogi sintezė iš 2-hidroksi-1-naftaldehido, įvairių diaminų ir vario (II) ar kobalto (II) acetatų.