

Nickel(II) and Copper(II) Complexes of a New Tetradentate Schiff Base Ligand: Synthesis, Characterization, Thermal Studies and Use as Precursors for Preparation of NiO and CuO Nanoparticles

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ABSTRACT: A new tetradentate N_2O_2 Schiff base ligand ($MeO-bph$)₂bn = *N,N'*-bis(2-hydroxy-4-methoxybenzophenone)-1,4-butanediamine was prepared from the condensation of butane-1,4-diamine with 4-methoxy-2-hydroxybenzophenone and characterized by ¹H-NMR spectroscopy and single crystal X-ray diffraction. Its nickel(II) and copper(II) complexes characterized using elemental analyses (CHN) and IR spectroscopy. Thermogravimetric analysis of the Schiff base ligand and its Ni(II) and Cu(II) complexes revealed their thermal stability and decomposition pattern. Finally, the complexes were used for the preparation of NiO and CuO nanoparticles by solid state thermal decomposition. The nanoparticles were characterized by FT-IR, XRD, and SEM. FT-IR and XRD confirmed the purity of the formed products NiO and CuO.

KEYWORDS: Nickel(II); Copper(II); Schiff base; Nanoparticles; XRD; SEM.

INTRODUCTION

Recent years, there has been enormous interest in the synthesis of nickel(II) and copper(II) Schiff base complexes because of their structural flexibility [1-5]. They adopt both tetrahedral and square planar geometries depending on steric and electronic effects of the Schiff base ligands [1-15]. Tetradentate N_2O_2 Schiff base ligands act as good chelating ligands for transition metal

ions [6-15] and they can form stable square-planar nickel(II) [16,17] and copper(II) [18,19] complexes. Recently, thermal decomposition of Schiff base complexes have been extensively studied [5-8] because of their role in the development of coordination chemistry possible application as precursors for the preparation of transition metal oxide nanoparticles [20-22].

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The transition metal oxide nanoparticles have versatile application and properties [23-26]. Among them, NiO and CuO nanoparticles have received much attention [27-34]. Nanoparticles of NiO, as an important p-type semiconductor with a wide band gap, can be used to photocatalysis [29], supercapacitors [30] and as anode materials for Li-ion batteries [28]. Moreover, they are cheap and abundant in nature [27]. Copper oxide (CuO), as a p-type semiconductor with a narrow indirect band gap, has potential applications in the field of electro-reduction of CO₂ to ethanol [31], in Li-ion batteries [34], water purification [32] and also has interesting optical properties [33].

Recently, our group reported preparation of various transition metal oxide nanoparticles from their Schiff base complexes [20-22]. Herein we report the synthesis, characterization and thermal studies of nickel(II) and copper(II) complexes with a new tetradentate Schiff base ligand (MeO-bph)₂bn = *N,N'*-bis(2-hydroxy-4-methoxybenzophenone)-1,4-butanediamine (Scheme. 1) and preparation of NiO and CuO nanoparticles by their solid-state thermal decomposition.

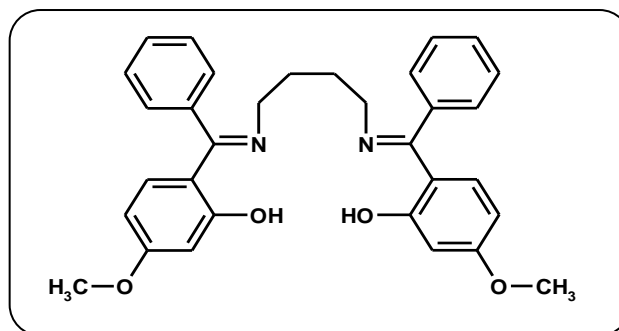
EXPERIMENTAL SECTION

Material and method

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer, and results agreed with calculated values. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on a FT-IR Perkin-Elmer spectrophotometer. The ¹H NMR spectrum was recorded on a BRUKER DRX-400 AVANCE spectrometer at 300 MHz for the Schiff base ligand. All chemical shifts are reported in δ units downfield from TMS. The TG/DTA was performed on a Perkin Elmer TG/DTA lab system 1 (Technology by SII) in a nitrogen atmosphere with a heating rate of 20 °C/min in the temperature span of 50–800 °C. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-K α radiation with nickel beta filter in the range $2\theta = 10^\circ$ – 80° . The Scanning Electron Microscopy (SEM) images were obtained from a Philips XL-30ESEM.

X-ray structure determination

A single crystal of the dimensions 0.85 mm \times 0.54 mm \times 0.29 mm was chosen for the X-ray diffraction study.



Scheme 1: Chemical structure of the tetradentate Schiff base ligand (MeO-bph)₂bn.

Crystallographic measurements were done at 120 K with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., with mirrors-collimated Mo-K α radiation. The crystal structure was easily solved by charge flipping with program SUPERFLIP [35] and refined with the Jana2006 program package [36] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by Diamond 4.0 [37]. All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice H atoms bonded to C were kept in ideal positions with C–H = 0.96 Å while positions of H atom bonded to N were refined freely. In both cases, $U_{iso}(H)$ was set to $1.2U_{eq}(C,N)$. All non-hydrogen atoms were refined using harmonic refinement. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

Preparation of (MeO-bph)₂bn

A solution of 1,4-butanediamine (0.88 g, 0.01 mol) in 15 mL ethanol is added drop-wise to a ethanolic solution of 2-hydroxy-4-methoxybenzophenone (0.46 g, 0.02 mol) under stirring condition. The reaction mixture is then refluxed for 12 h when the solution color turns yellow. Microcrystals of (MeO-bph)₂bn was filtered and washed by cold ethanol. Crystallization from a mixture of chloroform/methanol (1:1, v/v) has yielded good crystals. Anal. Calcd. for C₃₂H₃₂N₂O₄: C, 75.59%; H, 6.29%; N, 5.51%. Found; C, 75.58%; H, 6.34%; N, 5.55%. FT-IR (KBr, cm⁻¹): 2917-3051 (C–H aromatic and aliphatic), 2819 (–CH=N), 1576 (–C=N–). ¹H NMR (CDCl₃, ppm): 1.92-2.01 (q, 4H, C-CH₂-CH₂-C), 3.29-3.35 (t, 4H, N-CH₂-C-), 3.78 (s, 3H, CH₃O-), 6.09-6.14 (dd, 2H, Ar-H), 6.61 (d, 2H, Ar-H), 7.26-7.64 (m, 14H, Ar-H), 16.15 (s, 2H, Ar-OH).

Table 1: Crystallographic data and structural refinement details of (MeO-bph)₂bn.

Formula weight	C ₃₂ H ₃₂ N ₂ O ₄
Formula weight	508.6
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	13.7555 (6) Å
<i>b</i> , Å	8.1231 (3) Å
<i>c</i> , Å	11.9065 (5) Å
β , deg	103.747 (4)°
<i>wR</i> (<i>F</i> ²)	0.115
$\Delta\rho_{\max}$	0.27 e Å ⁻³
<i>V</i> , Å ³	1292.29 (9) Å ³
<i>Z</i>	2
μ , mm ⁻¹	0.09 mm ⁻¹
Measured reflections	12135
Measured independent	3217
<i>R</i> _{int}	0.021
Reflections with <i>I</i> > 3 σ (<i>I</i>)	2579
Parameters	175
<i>S</i>	1.69
<i>R</i> (<i>F</i> ² > 2 σ (<i>F</i> ²))	0.041
$\Delta\rho_{\min}$	-0.29 e Å ⁻³

Preparation of complexes

To 10 mL methanolic solution of 0.2 mmol NiCl₂·6H₂O or Cu(NO₃)₂·3H₂O, methanolic solution of (MeO-bph)₂bn (0.2 mmol) is added drop-wise under stirring condition. Stirring is continued for 2.5 h at 60 °C, and the solution is allowed to cool at room temperature. A powder of a complex is obtained by slow evaporation of solvent for several days. Several attempts to grow single crystals of the complexes were unsuccessful.

Anal. Calcd. for C₃₂H₃₀NiN₂O₄: C, 68.02%; H, 5.31%; N, 4.96%. Found; C, 68.05%; H, 5.36%; N, 5.01%. FT-IR (KBr, cm⁻¹): 2917-3051 (C-H aromatic and aliphatic), 2819 (-CH=N), 1576 (-C=N-).

Anal. Calcd. for C₃₂H₃₀CuN₂O₄: C, 67.19%; H, 5.25%; N, 4.90%. Found; C, 67.23%; H, 5.29%; N, 4.93%. FT-IR (KBr, cm⁻¹): 2917-3051 (C-H aromatic and aliphatic), 2819 (-CH=N), 1576 (-C=N-).

Preparation of nanoparticles

The Schiff base complexes were loaded into a platinum crucible, placed in an oven and heated at a rate of 10 °C min⁻¹ in air. Nanoparticles of NiO and CuO were obtained at 500 and 400 °C, respectively, after 3 h. The final products were washed by ethanol to remove impurities, if any, and dried at room temperature for several days. The synthesized NiO and CuO nanoparticles were characterized by FT-IR, XRD, and SEM.

RESULTS AND DISCUSSION

Elemental analyses of the Schiff base ligand (MeO-bph)₂bn and its nickel(II) and copper(II) complexes are presented in the experimental section. The results revealed the molar ratio of ligand and the metal ion was 1:1 with the corresponding formulas Ni{(MeO-bph)₂bn} and Cu{(MeO-bph)₂bn}. The Schiff base ligand (MeO-bph)₂bn is completely soluble in common organic solvents but the nickel(II) and copper(II) complexes are only soluble in coordinating solvents such as DMF and DMSO. The Schiff base ligand (MeO-bph)₂bn and its nickel(II) and copper(II) complexes are stable at room temperature in the solid state.

FT-IR and ¹H-NMR spectra

The FT-IR spectra are presented in Fig. 1. The ligand shows a strong band at 1576 cm⁻¹ that is assignable to the imine (-C=N-) stretching vibration. The vibrational frequency of this group appears at 1561 cm⁻¹ for the nickel(II) complex and at 1578 cm⁻¹ for the copper(II) complex. The vibrational frequency of the OH group in the free ligand appears at 3415 cm⁻¹, and it is absent in the complexes [20-22].

The Schiff base complexes were thermally decomposed in an electric furnace. The FT-IR spectra of the final residues (Fig. 2) confirmed the formation of NiO and CuO nanoparticles [20-22] by showing peaks at about 465 and 506 cm⁻¹ assigned to Ni-O and Cu-O stretching [20-22]. The peaks at 1599 and 3266 cm⁻¹ in the FT-IR spectrum of NiO nanoparticles are assigned to H₂O molecules adsorbed on the surface of nanoparticles [20-22].

Room temperature ¹H-NMR spectrum of the Schiff base ligand (MeO-bph)₂bn in CDCl₃ is presented in Fig. 3. The ligand shows two singlets in 16.15 ppm and in 3.78 ppm, which are assigned to OH and CH₃O- groups.

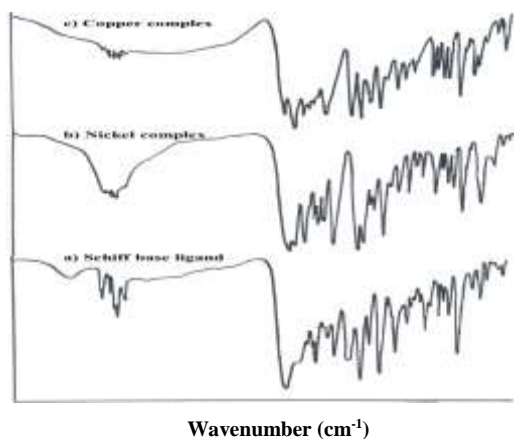


Fig. 1: FT-IR spectra of a) (MeO-bph)₂bn, b) nickel(II) and c) copper(II) complex.

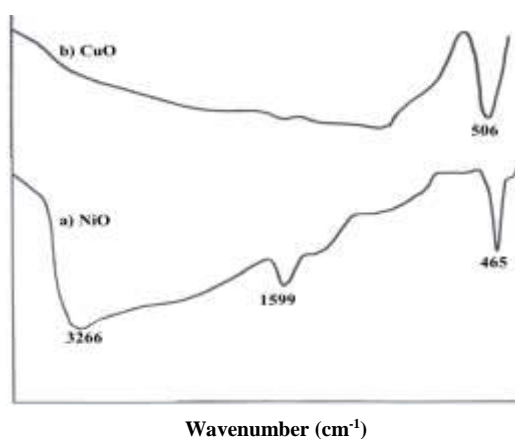


Fig. 2: FT-IR spectra of a) NiO and b) CuO nanoparticles obtained from complexes.

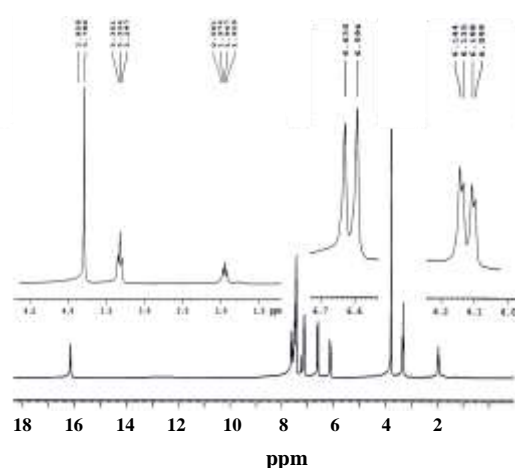


Fig. 3: ¹H-NMR spectrum of the Schiff base ligand (MeO-bph)₂bn.

Spectrum of the ligand shows other signals at about 1.92-2.01 (q, 4H, C-CH₂-CH₂-C), 3.29-3.35 (t, 4H, N-CH₂-C), 3.78 (s, 3H, CH₃O-), 6.09-6.14 (dd, 2H, Ar-H), 6.61 (d, 2H, Ar-H), 7.26-7.64 (m, 14H, Ar-H).

Crystal structure of the Schiff base ligand (MeO-bph)₂bn

The crystal structure of the Schiff base ligand (MeO-bph)₂bn was determined by X-ray single crystal diffraction analysis (Fig. 4). The ligand crystallized in the monoclinic space group *P2₁/c* with 2 molecules per unit cell. The bond distances N1=C7 (1.305(5) Å) and N1-C14 (1.459(6) Å) are within the interval reported for other similar Schiff bases derived from salicylaldehyde [38-41]. The whole molecule is generated by an inversion center located in the middle of the C-C bond of the butane segment and adopts an *E* configuration with respect to the C=N bond [40,41].

Thermal analysis of the ligand and its complexes

Thermal behavior (TG) of the Schiff base ligand (MeO-bph)₂bn and its nickel(II) and copper(II) complexes was studied under Ar atmosphere from room temperature to 800 °C with the heating rate of 20 °C per min. The TG curves are presented in Fig. 5. The decomposition of the ligand runs in one step, while complexes are decomposed two steps. The ligand shows a mass loss of 7% up to 305 °C, due to its partial decomposition. About this temperature a loss of 93% occurs in the temperature range of 305-800 °C, corresponding to the major stage of the decomposition [42]. The nickel(II) and copper(II) complexes are stable up to 200 and 225 °C, respectively, and during further heating they undergo decomposition in two stages. In the first stage, nickel(II) complex shows a mass loss of 20% in the temperature range 200 – 340 °C, while copper(II) complex shows a mass loss of 23% in the temperature range 200 – 340 °C. In the second stage, nickel(II) and copper(II) complexes show a mass loss of 65% and 62%, respectively, in the temperature range 340 – 800 °C. The final products of decomposition of nickel(II) and copper(II) complexes are nickel(II) oxide and copper(II) oxide, in the correspondence with the overall mass loss [8, 20-22].

XRD pattern

Fig. 6 shows the X-Ray Powder Diffraction (XRPD) pattern recorded in the 2θ range of 10° to 80° in Bragg-Brenano geometry. The powder profiles of the synthesized

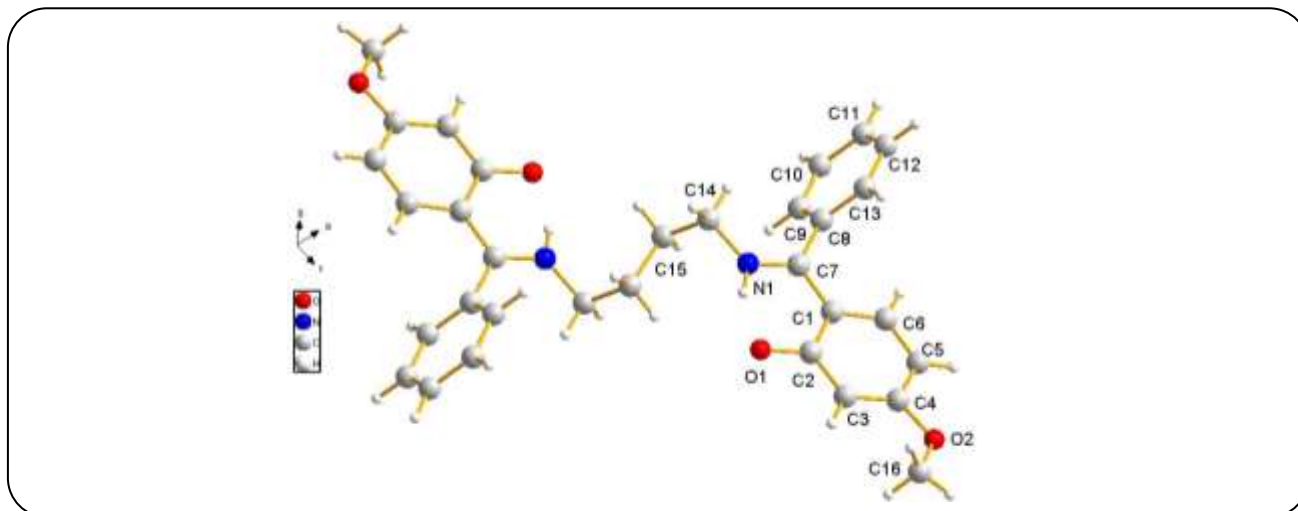


Fig. 4: ORTEP diagram of Schiff base ligand (MeO-bph)₂bn. Labels are given for the symmetry independent part of the molecule.

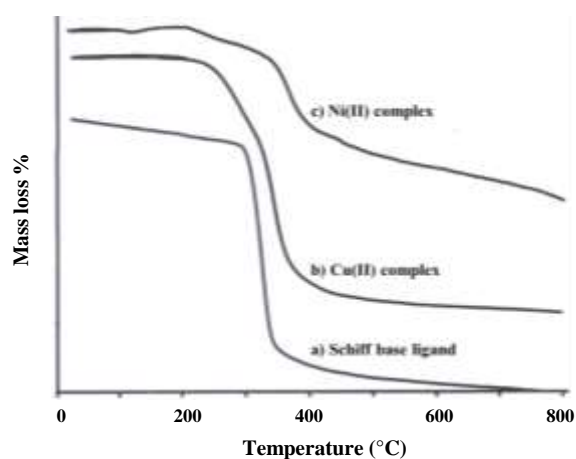


Fig. 5: The TG curves of a) Schiff base ligand b) copper(II) and c) nickel(II) complex.

nickel(II) and copper(II) oxides can be fully indexed on the basis of the hexagonal (Rh) NiO (JCPDS: 44-1159) [42,43,21] and the monoclinic CuO (JCPDS: 45-0937) [34]. XRPD results thus indicate the complete conversion of Schiff base complexes to NiO and CuO. No obvious impurities were detected, indicating the high phase purity of the as-prepared samples. Also, the broadening of all the peaks in the XRD patterns of NiO and CuO indicates that the crystallites are small. The average crystallite size of NiO and CuO nanoparticles was determined to be 17.7 and 19.4 nm, respectively, by using the Scherrer formula.

SEM images

Fig. 7 shows the typical SEM images of the as-prepared NiO and CuO nanoparticles at two different

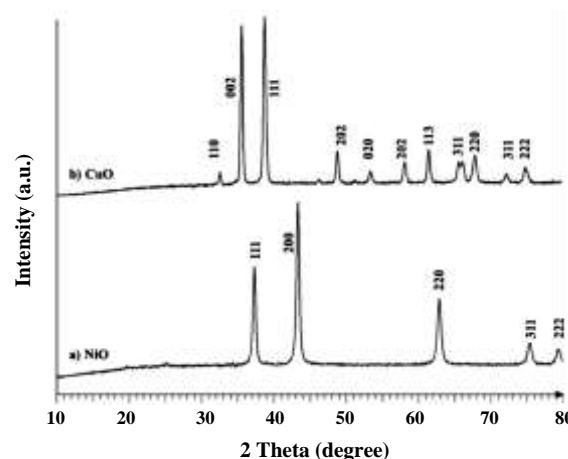


Fig. 6: XRD patterns of a) NiO and b) CuO nanoparticles.

scales. It can be clearly seen that the morphology of them is different from each other. The crystallite size and shape of NiO nanoparticles is quite different from that of CuO nanoparticles. The NiO nanoparticles are microcrystals with well-developed habitus while CuO consists of conglomerates of very small particles. This difference is however not reflected by the size derived from the Scherrer formula, probably because each conglomerate diffracts as a single grain

CONCLUSIONS

In summary, we have prepared NiO and CuO nanoparticles by a solid-state thermal decomposition of square-planar nickel(II) and copper(II) complexes. However, the crystallite size and shape of NiO

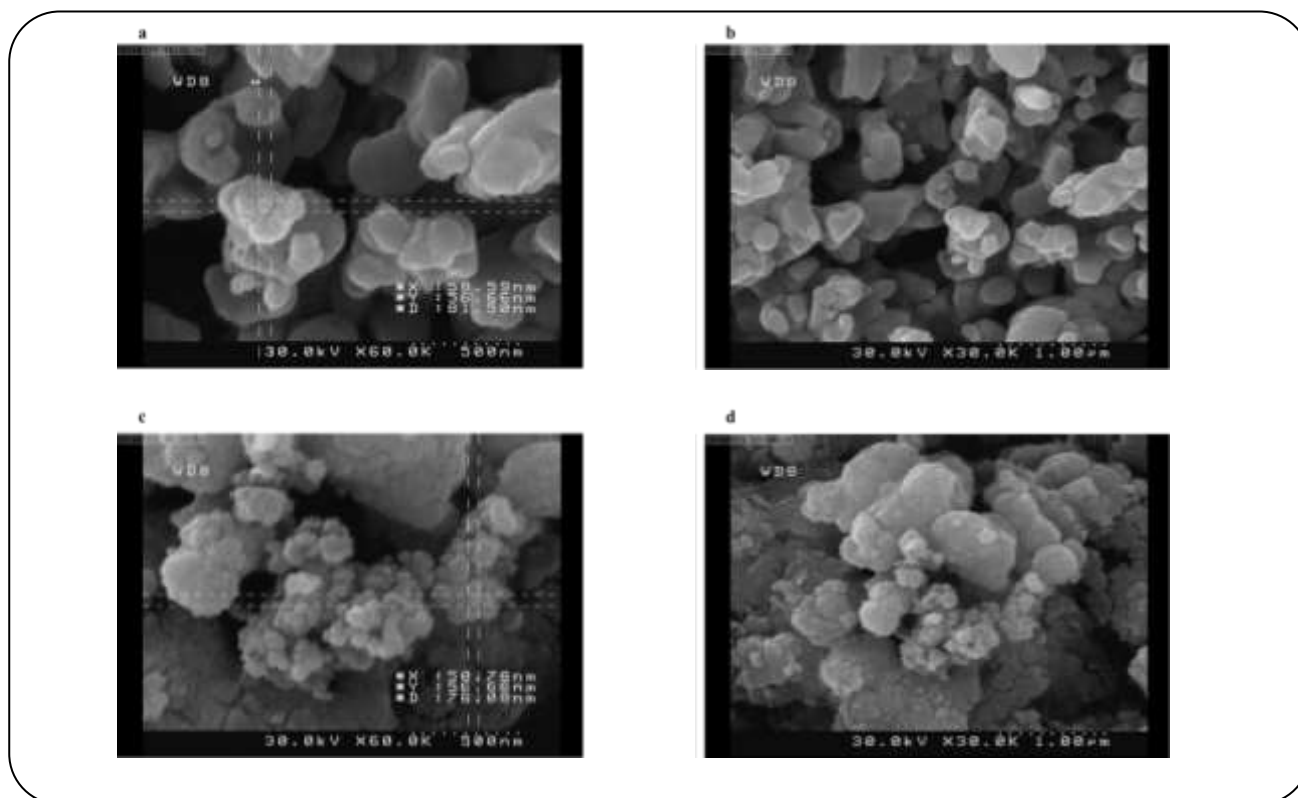


Fig. 7: SEM micrographs of the NiO (a,b) and CuO (c,d) nanoparticles at different scales

nanoparticles are quite different from that of CuO nanoparticles. This method is facile, nontoxic and inexpensive. Also, it can be used for other complexes.

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Appendix A. Supplementary material

CCDC 1588236 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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