

RESEARCH PAPER

Hydrothermal synthesis of copper (II) and nickel (II) nano-complexes with asymmetric tetradentate Schiff base ligand; A new precursor for preparation of copper (II) and nickel (II) oxide nanoparticles

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ABSTRACT

Two new nano-particles of copper (II) and nickel (II) complexes, [Cu(cd5ClSalen)] (1) and [Ni(cd5ClSalen)] (2) with unsymmetrical tetradentate Schiff base ligand cd5ClSalen={methyl-2-[N-[2-(2-hydroxy-5-chloro-2-phenyl) methylidynetrilo] ethyl]amino-1-cyclopentenedithiocarboxylate}, were synthesized by hydrothermal method. These compounds were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (IR), and elemental analysis. The complexes (in bulk) have a NNOS coordination sphere, with two nitrogen atoms coordinated in a cis configuration. The coordination around nickel center is essentially square-planar with a small tetrahedral distortion and the geometry around the copper center is square planar. Nano-particles of copper (II) and nickel (II) oxides have been prepared by calcination of two different copper (II) and nickel (II) complexes at 450 °C that were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and IR spectroscopy. The average size of the particles was estimated from the Sherrer formula. This study demonstrates that the Schiff base complexes may be suitable precursors for the preparation of nanoscale materials with different and interesting morphologies.

How to cite this article

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INTRODUCTION

Schiff bases are important ligands in coordination chemistry with extensive applications in different fields. Schiff bases are derived from aromatic carbonyl compounds and have been widely studied in connection with metalloprotein models and asymmetric catalysis, due to versatility of their steric and electronic properties [1]. Nanometer-sized particles of metal coordination supramolecules are fascinating to explore, since their unique properties are controlled by the large number of surface molecules, which experience an entirely different environment than those in a

bulk crystal. Controlling the growth of materials at the submicrometer scale is of central importance in the emerging field of nanotechnology [2-10]. Although considerable effort has been dedicated to the controlled synthesis of nanoscale particles of metals, oxides, sulfides, and ceramic materials, little attention has been focused to date on nanoparticles of supramolecular compounds such as Schiff base complexes. Hydrothermal method is a promising synthetic method because of the low process temperature and very easy control of the particle size. The hydrothermal process has several advantages over other growth processes such as

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use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazard [11]. In the present work, two copper (II) and nickel (II) supramolecules with ligand {methyl-2-[N-[2-(5-chloro-2-phenolate) methylidynetriolo] ethyl] aminato (-1)-1-cyclopentenedithiocarboxylate, were synthesized by hydrothermal method. Copper (II) oxide nanoparticles has wide different applications according to the physical and chemical properties, such as superconductivity, photovoltaic properties, relative stability, and the antimicrobial activity [12]. Nowadays, application of CuO nanoparticles is of particular importance for antioxidant [13], antibacterial [14], thermal conductivity [15], battery [16], and solar cell applications [17]. CuO-NPs has been prepared via several methods such as sonochemical [18], alcohol-thermal and colloid-thermal synthesis [19-21], electrochemical method [22-24], and microwave radiation method [2]. Nickel oxide has a wide range of application in the manufacture of ceramic composite parts, magnetic materials, alkaline battery cathodes, anti-ferromagnetic layers and p-type transparent conducting films, electrochromic films, heterogeneous catalytic materials and gas sensors [26-32]. NiO nano-powder has been prepared using several methods such as ultrasonic radiation, carbonyl method, laser chemical processing, microwave pyrolysis, sol-gel technique and mechanochemical processing [33-41]. The use of coordination complexes as precursors for the preparation of inorganic nanomaterials such as copper (II) and nickel (II) oxide has not yet been investigated thoroughly. In this paper, copper (II) and nickel (II) oxide nanoparticles were obtained by direct thermal decomposition of compounds 1 and 2 at 450 °C. The preparation of metal oxide nanostructures through thermal decomposition of complexes opens a new window for chemists to overcome challenges such as control of process condition, particle size, particle crystal structure and purity.

EXPERIMENTAL SECTION

Materials and Physical Techniques

All reagents and solvents for the synthesis and analysis were commercially available from Merck Company and used as received. Doubly distilled water was used to prepare aqueous solutions. A 30 ml Teflon-lined stainless-steel autoclave was used to do the reactions. The vessels were filled

approximately to 40% capacity and heated for 4 h at 180 °C. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Micro analyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips company with monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Simulated XRD powder pattern based on single crystal data were prepared using Mercury software [42]. The crystallite sizes of the selected samples were estimated using the Sherrer method. The samples were characterized with a scanning electron microscope (SEM) (Philips XL 30) with gold coating.

Synthesis of ligand *cd5Clsalen*, [*Cu(cd5Clsalen)*] (1) and [*Ni(cd5Clsalen)*] (2)

Methyl-2-{N-(2'-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) was prepared by published methods [43-46]. The ligand was prepared by addition of the equimolar amount of the 5-chlorosalicylaldehyde, to a methanolic solution of Hcden. The yellow product was recrystallized from methanol/chloroform 1:1 (V:V). To a solution of an appropriate amount of ligand (0.1 mmol) in 10 mL of chloroform/methanol 2:1 (V:V), a solution of metal (II) acetate (0.1 mmol) in 10 mL of methanol was added. The solution was stirred for 15 min and then allowed to stand at room temperature for 24 h. After filtering, the crude product was recrystallized from acetonitrile/methanol 1:1 (V:V).

Compound 1: White crystals, d.p. 260 °C. Found C: 45.98, H: 4.39, N: 6.68, S: 15.12 %; calculated for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{ClO}_5\text{S}_2\text{Cu}$; C: 46.15, H: 4.11, N: 6.73, S: 15.40 %. IR (cm^{-1}) selected bands: $\nu = 710(\text{vs}), 1166(\text{s}), 1260(\text{vs}), 1455(\text{vs}), 1629(\text{s})$.

Compound 2: White crystals, m.p. 250 °C. (Found C: 46.42, H: 4.21, N: 6.83, S: 15.43 %; calculated for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{ClO}_5\text{S}_2\text{Ni}$; C: 46.69, H: 4.31, N: 6.66, S: 15.24 %). IR (cm^{-1}) selected bands: $\nu = 712(\text{vs}), 1150(\text{s}), 1260(\text{vs}), 1460(\text{vs}), 1629(\text{s})$.

Synthesis of [*Cu(cd5Clsalen)*] (1) and [*Ni(cd5Clsalen)*] (2) nano-particles using hydrothermal method

To prepare nano-scale compounds 1 and 2, to a solution of an appropriate amount of ligand (0.1 mmol) in 10 mL of chloroform/methanol 2:1 (V:V), a solution of metal (II) acetate (0.1 mmol) in 10 mL of methanol was added. The solution was

charged into a Teflon-lined stainless steel autoclave and heated at 450 °C for 24 h, then the autoclave was cooled to room temperature. The product was filtered, dried and characterized.

Compound 1: d.p. 253 °C. Found C: 45.49, H: 4.14, N: 7.04, S: 15.93 %; IR (cm⁻¹) selected bands: ν = 710(vs), 1164(s), 1260(s), 1455(vs), 1629(s).

Compound 2: m.p. 244 °C. (Found C: 46.27, H: 4.13, N: 6.35, S: 15.19 %; IR (cm⁻¹) selected bands: ν = 715(vs), 1150(s), 1260(s), 1460(vs), 1629(s).

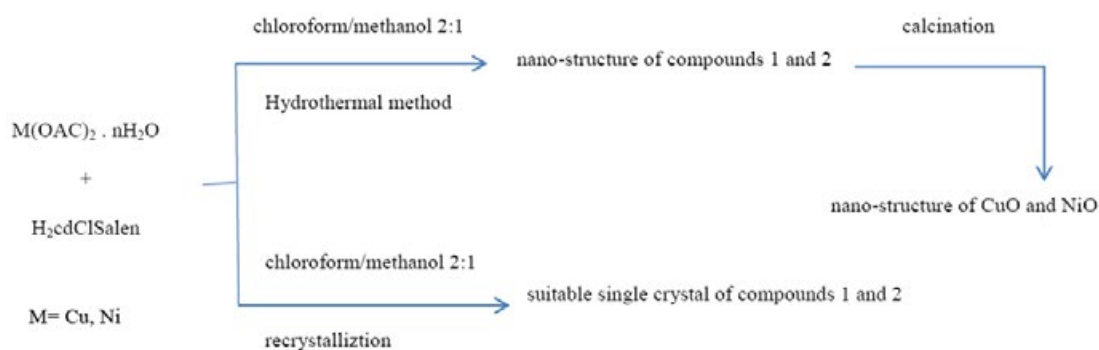
Synthesis of CuO and NiO nanoparticles

For preparation of CuO and NiO nano-particles calcinations of bulk powder compounds 1 and 2 were done at 450 °C in static atmosphere of air for 4 h. IR spectrum and powder XRD diffraction shows that calcination was completed and the entire compounds decomposed.

RESULTS AND DISCUSSION

Reaction between tetradentate Schiff base ligand cd5ClSalen and copper (II) or nickel (II) acetate yielded crystalline materials formulated as [Cu(cd5ClSalen)] (1) and [Ni(cd5ClSalen)]

(2), respectively. Nano-particles of compounds 1-2 were obtained by hydrothermal method while the bulk powder of compounds 1-2 were obtained using reflux method. Scheme 1 gives an overview of the methods used for the synthesis of compounds 1-2 using the two different routes. The elemental analysis of the nanoparticles and single crystalline materials of compounds 1 and 2 are indistinguishable. The FT-IR spectra of two complexes 1-2 compared with those of the corresponding ligand indicates that the ν (C=N) band around 1600 cm⁻¹ ν (C-O) bands at 1220-1286 cm⁻¹ ν (C=C) band in the region of 1456-1496 cm⁻¹ ν (C-S) band at 700-790 cm⁻¹ and ν (C-S) + ν (C-N) cm⁻¹ bands between 1099 and 1180 cm⁻¹ are shifted to lower energies. These results showed that the Cu (II) and Ni (II) ions are coordinated through the nitrogen atoms of the amine group, oxygen atom of the phenolic group and sulfur of the C=S group for two complexes. Figs. 1 and 2 show the comparison of XRD patterns, simulated from single crystal X-ray data against the nano powder of compounds 1-2 prepared by the hydrothermal method, respectively. The comparison between



Scheme 1. Materials produced and synthetic methods

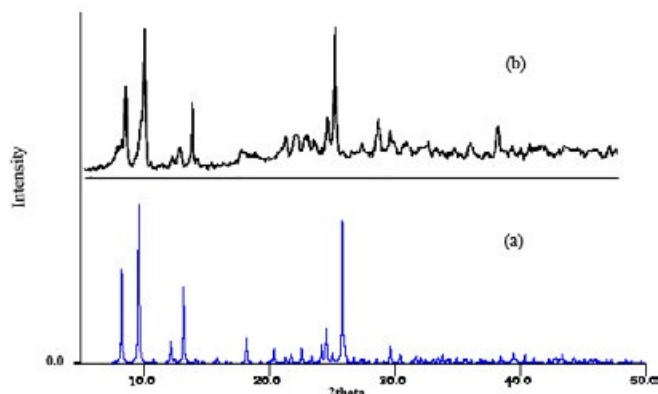


Fig. 1. XRD patterns: (a) simulated pattern based on single crystal data of compound 1, (b) nano-particles of compound 1

these XRD patterns indicates acceptable matches with slight differences in 2θ . Estimated from the Sherrer formula for the calculation of particle sizes from the broadening of the XRD peaks ($D = 0.891\lambda / \beta \cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively), the average size of the particles was found to be around 92.4 for compound 1 and 76.3 for compound 2. Figs. 3 and

4 show the SEM images of the compounds 1 and 2. The structures of compounds [Cu(cd5Cl salen)] (1) and [Ni(cd5Cl salen)] (2) were previously analyzed and reported [47-48]. In compound 1, the Cu (II) atom is coordinated by S, O and two N atoms in a nearly planar environment. The coordination geometry around Cu center is nearly planar with the dihedral angle of $7.65(3)^\circ$ between planes of NCuO and NCuS (. The x-ray structure of compound 2 revealed that the complex has a N_2OS

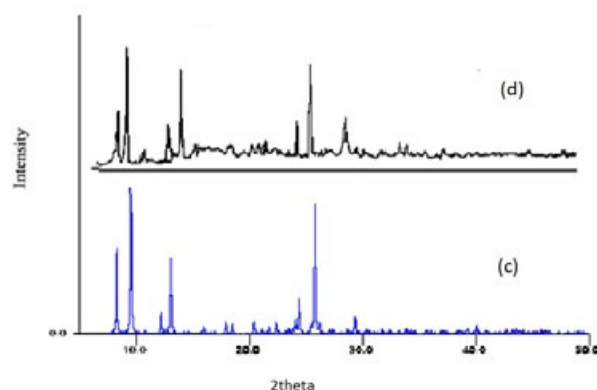


Fig. 2. XRD patterns: (c) simulated pattern based on single crystal data of compound 2, (d) nano-particles of compound 2

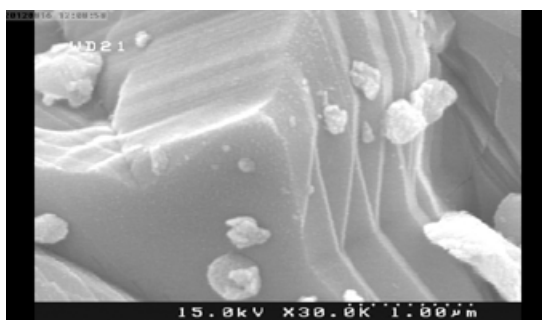


Fig. 3. SEM photograph of [Cu(cd5Cl salen)] (1) nano-particles prepared by hydrothermal method

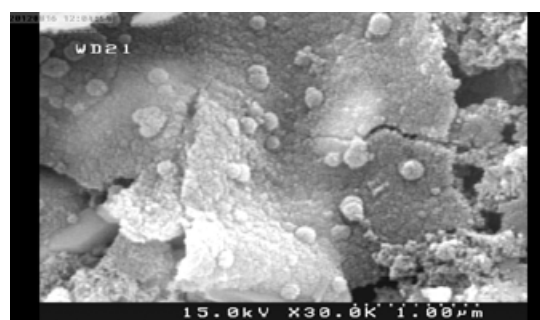


Fig. 4. SEM photograph [Ni(cd5Cl salen)] (2) nano-particles prepared by hydrothermal method.

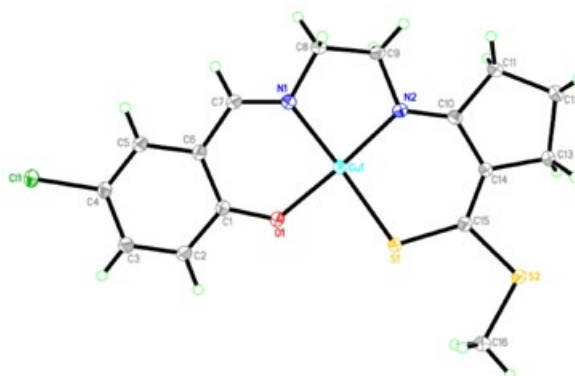


Fig. 5. ORTEP diagram and atom numbering scheme for the complex [Cu(cd5Cl salen)] with 50% probability ellipsoid for the non-hydrogen atom.

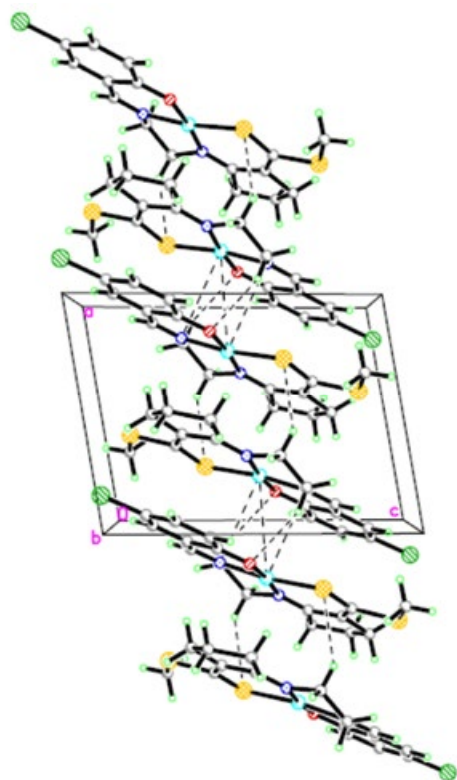


Fig. 6 The crystal packing of the [Cu(cdClsalen)] complex showing one-dimensional infinite chain along the *a*-axis

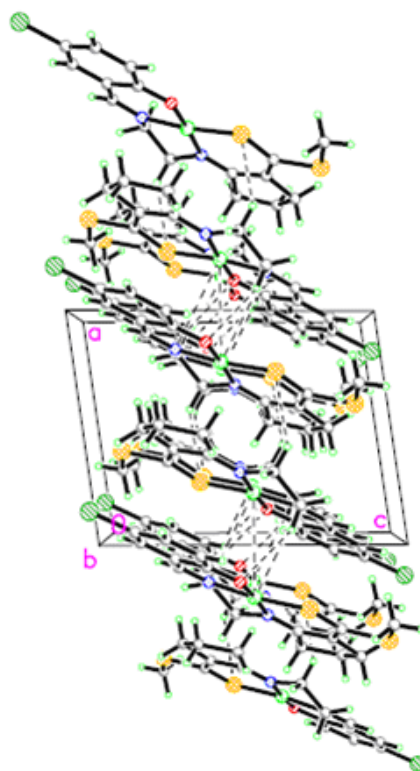


Fig. 8. The crystal packing in [Ni(cd5-ClSalen)], showing one-dimensional infinite chain along the *a*-axis. Intermolecular interactions are shown as dashed lines.

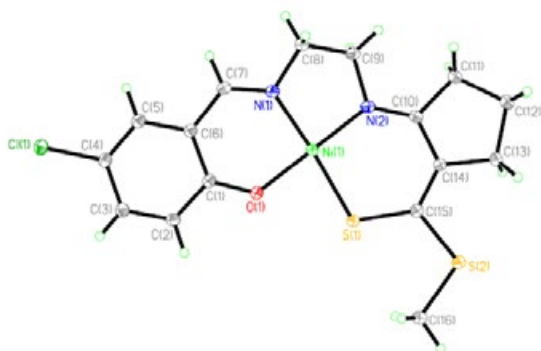


Fig. 7 Molecular structure of the complex [Ni(cd5-ClSalen)] with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

coordination sphere, with the two nitrogen atoms coordinated in a cis configuration (Figs. 5 and 6). The coordination around nickel is essentially square-planar with a small tetrahedral distortion. (Dihedral angle of $5.43(3)^\circ$ between coordination planes NNiO and SNiN (Figs. 7 and 8).

Nano-particles of CuO and NiO have been generated by calcination of compounds 1 and 2. The final product upon calcination of compounds

1-2 at 400°C , based on their IR and XRD patterns are CuO and NiO. The IR spectrum of CuO and NiO nanoparticles after calcinations of compounds 1-2 shows absorption bands at about 500 cm^{-1} that can be attributed to the stretching modes of M-O ($\text{M}=\text{Cu}$ and Ni) and the weak bands in the range of $1380\text{-}3425\text{ cm}^{-1}$ are probably attributed to the presence of water in the KBr matrix. Figs. 9 and 10 show X-ray powder diffraction pattern of CuO and NiO nanoparticles after calcination of compounds 1 and 2. The XRD patterns of CuO and NiO nanoparticles after calcinations of compounds 1 and 2 are in agreement with the typical CuO diffraction (monoclinic phase, space group C2/c , with lattice constants $a = 4.5850\text{ \AA}$, $b = 4.230\text{ \AA}$ and $c = 5.2000\text{ \AA}$, $Z = 4$, ICSD No. 00-041-0254) and NiO diffraction (cubic phase, space group $\text{Fm}\bar{3}\text{m}$, with lattice constant $a, b, c = 4.1771$ and $z = 4$, ICSD No. 00-047-1049). No characteristic peaks of impurities are detected in XRD patterns. Figs. 11 and 12 show the SEM images and the corresponding particle size distribution histogram of CuO and NiO nanoparticles obtained from calcinations of nano compounds 1-2 at 450°C .

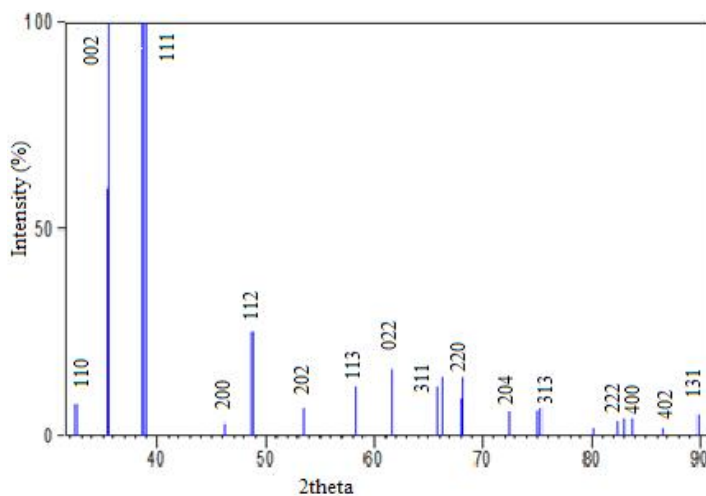


Fig. 9 XRD pattern of CuO nanoparticles prepared by calcinations of nano-powder of compound 1

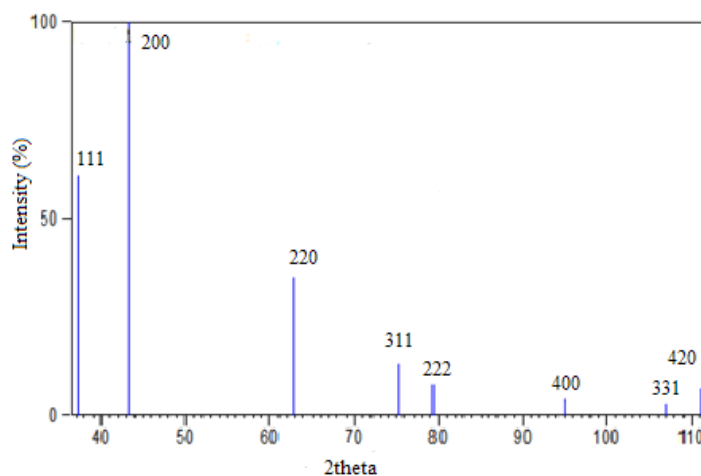


Fig. 10. XRD pattern of NiO nano-particles prepared by calcinations of nano-powder of compound 2

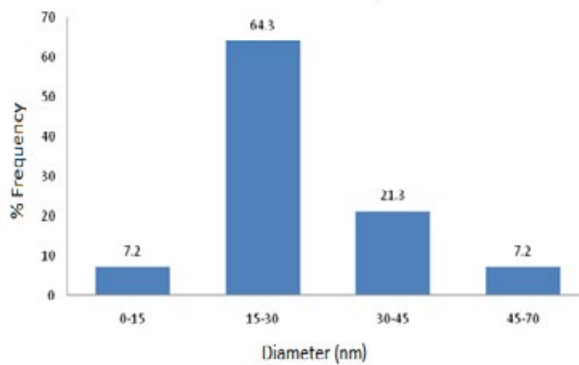
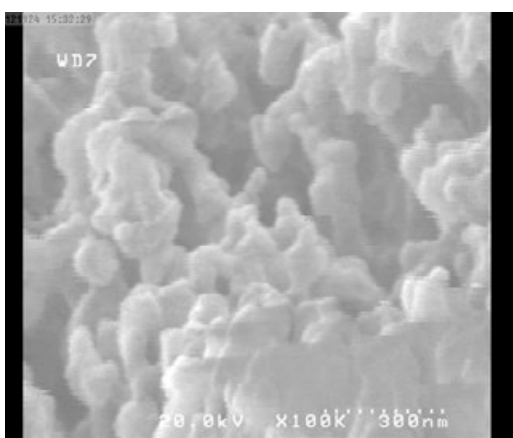


Fig. 11. SEM image and the corresponding particle size distribution histogram of CuO nano-particles prepared by calcination of nano-powder of compound 1 at 450 °C

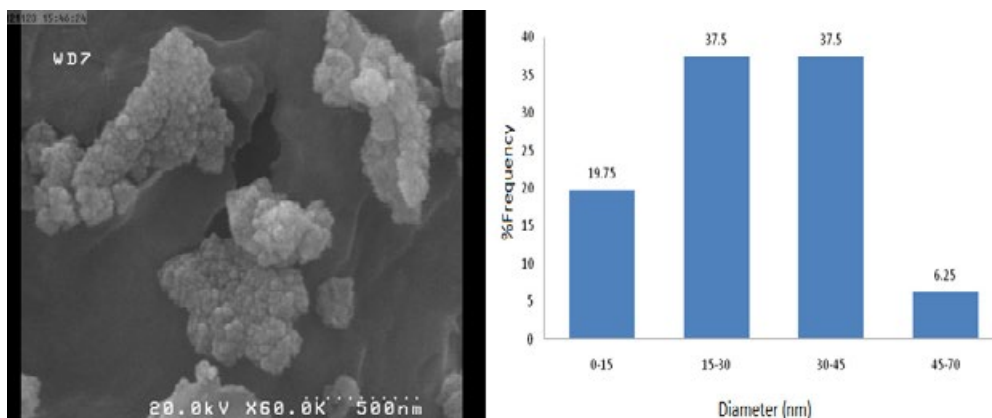


Fig. 12. SEM image and the corresponding particle size distribution histogram of NiO nano-particles prepared by calcination of nano-powder of compound 2 at 450 °C

CONCLUSION

Nano particles of copper (II) and nickel (II) complexes with a tetradentate Schiff base ligand, [[Cu(cd5Cl salen)] (1) and [Ni(cd5Cl salen)] (2), have been synthesized by hydrothermal method. Compounds 1-2 were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD), elemental analyses and IR spectroscopy. Nano-particles of copper (II) and nickel (II) oxide have been prepared by calcinations of two different Schiff base complexes, compounds 1-2. The nano oxides were characterized by scanning electron microscopy (SEM) images, X-ray powder diffraction (XRD) and IR spectroscopy. This study demonstrates that the Schiff base complexes may be suitable precursors for the preparation of nanoscale materials with interesting morphologies.

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CONFLICT OF INTEREST

The author declare that there is no conflict of interests regarding the publication of this manuscript.

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