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SYNTHESIS, AND SPECTROSCOPIC CHARACTERIZATIONS OF GOLD(III) COMPLEXES CONTAINING NITROGEN-HETEROCYCLE BASED PYRIDINE DERIVATIVES AS A BIOMOLECULAR CHELATES

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ABSTRACT. Three gold(III) nanostructured complexes of nicotinamide (nta), picolinic acid (pica), and isonicotinic acid (inta) were synthesized by the reacted of $AuCl_3$ salt with nta, pica, and inta with 1:2 stoichiometry in the alcoholic medium. The solid products obtained were formulated by comparing experimental and calculated data for microanalytical (C, H, N) and metal. Both produce 1:2 compounds with metal ions. The prepared complexes were characterized by different physico-spectroscopic techniques. The FTIR, and ^{1}H NMR spectral analysis, morphological analysis (scanning electron microscopy SEM, transmittance TEM, and X-ray powder diffraction XRD) of these complexes have been discussed. The conductive behavior of the complexes indicates that all of them behave as electrolytic behavior. The mononuclear gold(III) complexes have formulated as $[Au(nta)_2(Cl)_2].Cl$, $[Au(pica)_2].Cl$ and $[Au(inta)_2].Cl$. The shifts of the ν(N–H) amino, ν(C=N) pyridine, and ν(C=O) carboxylic stretches have been monitored to find out the donor sites of the ligands. According to the experimental data, the three complexes can be characterized in the solid state as mononuclear, with a four-coordinate stereochemistry.

KEY WORDS: Gold complex, Nicotinamide, Picolinic acid, Isonicotinic acid, Nanostructure, Spectroscopic

INTRODUCTION

Metal ions are not only paramount for all living systems but also have a vital role in biological systems such as micronutrients. Metal ions are an important part in a lot of organs of animals such as blood, bones, teeth, nerves, some proteins, and enzymes. Metals are mostly coordinated in the living bodies to other chemical species [1]. Vitamins on the other hand are accessory dietary factors and taken in small amounts. Vitamins help animals to make specific metabolic processes and physiological functions that are vital to life [2, 3]. Water-soluble B-vitamins niacin is one of them, which is converted to nicotinamide coenzyme in the blood, brain, kidney, and liver. Provitamin of niacin tryptophan is an amino acid. Research on metal with vitamin B complexes for few years was done [4-6]. The preparation of complexes of some toxic metal with nicotinamide and nicotinic acid in solid phase and their characterisation using distinct conventional methods and studies of their various properties with an objective to establish the nature of metal-vitamin B3 interactions were studied. For many biological systems, pyridine ring plays a significant role as in iso nicotinic acid, nicotinamide, picolinic acid and nicotinic acid. The derivatives of pyridine possess some biological properties such as antitumor and antibacterial activity [7]. The monocarboxylic acids containing pyridine have amphoteric characters that have biological interest. Some of these derivatives have physiological activity; for example, nicotinamide is the pellagra preventative factor for complex vitamin B2 and the newly discovered anti-tuberculosis drug iso nicotinic acid hydrazide [8]. Nicotinamide acts as coenzyme, nicotinamide adenine dinucleotide (NAD). Nicotinamide has a vital role in the living cells metabolism and are biologically active like antibacterial or insulin mimetic [9]. The structure of nicotinamide has been studied [10, 11]. For 2-pyridinecarboxylic acid known as picolinic acid, has carboxylic group in

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ortho-position to N-atom in the pyridine ring, and coordinate as bidentate ligand via nitrogen atom and oxygen atom of carboxylate group. In tryptophan degradation pathway picolinic acid is formed in the body as an intermediate and approved as food supplement. Chromax, is the trademark name for $Cr(pic)_3$ complex, which has been shown to assist diabetic patients in maintaining glycemic control [12]. The crystalline structures for 2-picolinic acid with some transition metal ions have been studied [13-17]. For 4-pyridinecarboxylic acid known as isonicotinic acid which act as an isomer for picolinic acid and nicotinic acid and has COOH group at the position 2 and 3 respectively in comparison with 4-position for isonicotinic acid. There are only a few studies concerning properties of insulin mimetic of picolinate complexity and possess methyl group that act as electron-donating groups [18]. Picolinate compounds can form mononuclear or polynuclear complexes owing to their ability to form a chelating ring. They also can act as bridging ligands [19], thus can act as building blocks. Palladium mononuclear new complexes prepared by reaction of $PdCl_2$ with nicotinamide, picolinic acid, and isonicotinic acid have been isolated prepared with 1:2 M ratio forming new complexes of $[Pd(nicotinamide)_2(Cl)_2]$, $[Pd(picolinic\ acid)_2]$, and $[Pd(iso\ nicotinic\ acid)_2]$ [20]. Nicotinamide and nicotinic acid reacted with Cd(II), Hg(II) and Pb(II) in the aqueous medium [21]. The obtained solid products were characterized using different physicochemical tools UV-Vis, IR spectral analysis and thermal analysis. The conductance measurements for complexes refer to the fact that all complexes act as weak electrolytes.

The present work includes the preparation of complexes of gold(III) metal ions with nicotinamide (nta), picolinic acid (pica), and isonicotinic acid (inta) in solid phase and their characterization using different conventional methods and studies of their various properties in order to establish the nature of gold-chelate interactions.

EXPERIMENTAL

Reagents and apparatus

The chemicals presented in this study are pure analytical grade and received from Sigma-Aldrich Chemical Corporation, St. Louis, Mo, USA. These chemicals are summarized as: $AuCl_3$, nicotinamide, picolinic acid and isonicotinic acid.

Instrumentals

The contents of C, H, and N were measured using a Perkin Elmer CHN 2400 (USA). Electrolytic or non-electrolytic character for the prepared compounds were determined by using 1.0×10^{-3} mol/cm^3 dimethyl sulfoxide (DMSO) solutions, were measured using Jenway 4010 conductivity meter. FTIR measurements were measured on Bruker FTIR Spectrophotometer (4000–400 cm^{-1}). The ^{1}H-NMR spectra were measured on Varian mercury VX-300 NMR spectrometer and run at 300 MHz spectra in deuterated (DMSO-d_6). Scanning electron microscopy (SEM) images were taken in Quanta FEG 250 equipment. The X-ray diffraction patterns were recorded on X 'Pert PRO PAN analytical X-ray powder diffraction, target copper with secondary monochromate. The transmission electron microscopy images (TEM) were performed using JEOL 100s microscopy.

Synthesis

Gold(III) complexes of nicotinamide (nta), picolinic acid (pica) and iso nicotinic acid (inta) were prepared according to the following procedure: A 0.197 g (1 mmol) of $AuCl_3$ was dissolved in 20 mL methanol then 20 mL of methanolic solution of 2 mmol of ligands (nicotinamide (nta), picolinic acid (pica) and isonicotinic acid (inta)) were added to the methanolic $AuCl_3$ solution. The yellow-to-brown color changes were recorded. The mixtures were stirred using magnetic

stirrer for 4 h. The Precipitated solid compounds were filtered, washed with methanol, and dried over $CaCl_2$ in a desiccator.

RESULTS AND DISCUSSION

Elemental analysis and conductance studies

The elemental analysis data suggests that, the gold(III) complexes have 1:2 stoichiometry (Table 1). Au(III) complexes have a crystalline structure and are soluble in warming DMSO and DMF organic solvents. The values of molar conductance for these complexes at the concentration of 10^{-3} M are in the range of 45-60 $\Omega^{-1}cm^2mol^{-1}$. The significant values for Au(III) compounds can be regarded as an electrolytes [22]. According to microanalytical and conductometric analysis data the complexes formula may have the following structures: $[Au(nta)_2(Cl)_2].Cl$, $[Au(pica)_2].Cl$ and $[Au(inta)_2].Cl$ as displayed in Figure 1.

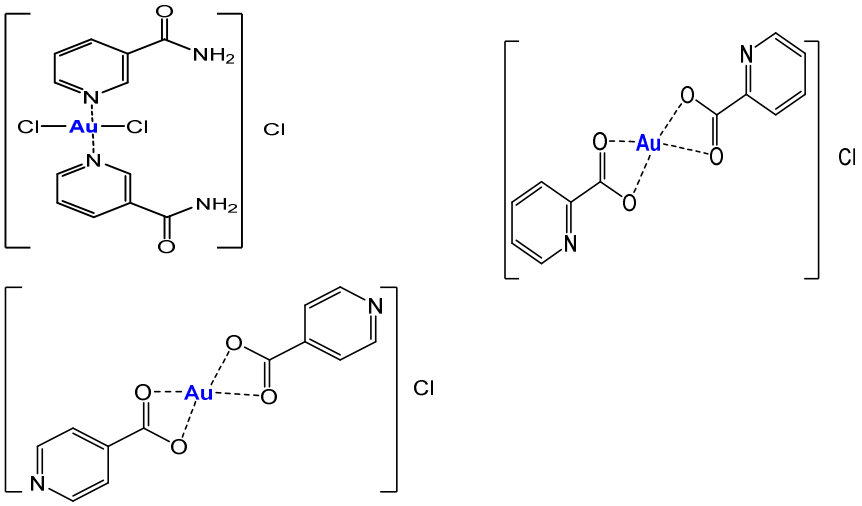


Figure 1. Speculated molecular structures of gold(III) complexes.

Table1. Elemental analysis and conductance data determined for gold(III) complexes.

Complexes	M.Wt (g/mol)	Λm ($\Omega^{-1}cm^2mol^{-1}$)	Elemental analysis, found (calculated) %			
			C	H	N	Cl
$[Au(nta)_2(Cl)_2].Cl$	548	60	(26.32) 25.92	(2.21) 2.18	(10.23) 10.17	(19.42) 19.33
$[Au(pica)_2].Cl$	577	45	(30.24) 30.02	(1.69) 1.62	(5.88) 4.82	(7.44) 7.26
$[Au(inta)_2].Cl$	577	51	(30.24) 30.11	(1.69) 1.63	(5.88) 5.79	(7.44) 7.31

FTIR spectra

By comparing the IR spectra for Au(III) complexes (Figure 2) with the data assignments that are listed in (Table 2), the mode of chelation of Au(III) complexes can be obtained. For free nicotinamide (nta) the stretching vibration band for the amide group υ(N–H) appeared at 3375 and 3157 cm^{-1} [23-25]. After chelation, these bands are shifted to 3420–3150 cm^{-1} range, and this

can be due to formation of H-bond between -NH_2 and -C=O. This deduced that the υ(NH) for Au(III)–nta complex has no any change, compared to free nta, confirming that -NH_2 does not participated in chelation. In the 2900–3100 cm^{-1} the medium-to-weak bands are assigned to υ(C–H) aromatic and aliphatic stretching vibrations. For free nicotinamide stretching vibration for -C=O of amido group appearing at 1699 cm^{-1}, while for Au(III) nta complex, at 1702 cm^{-1} a strong band with similar observation have been appeared which may be due to conjugation between -C=O group and pyridine ring under the effect of intermolecular H-bond [24]. The bands appeared at 1612 cm^{-1} and 1255 cm^{-1} due to stretching vibrations of υ (C=N) and υ (C–N), which are shifted to lower wavenumbers (1600–1604 cm^{-1} and 1205–1191 cm^{-1}) compared to free nta. The appearance of new bands at 603, 545 and 460 cm^{-1} in the spectra of the Au(III) complex, confirm the coordination of Au(III) via nitrogen atom of nicotinamide ligand which was assigned to υ(M–N).

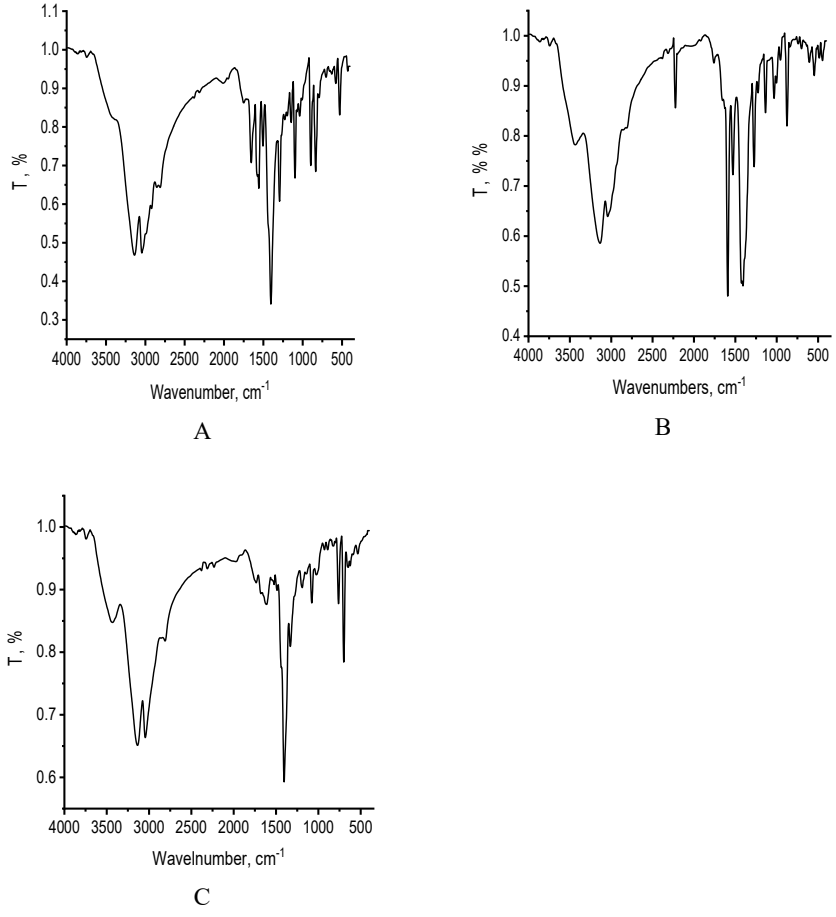


Figure 2. FTIR spectra of (A): $[Au(nta)_2(Cl)_2].Cl$, (B): $[Au(pica)_2].Cl$ and (C): $[Au(inta)_2].Cl$ complexes.

By making a comparison for IR spectra of the picolinic acid free ligand that reveals a considerable change in frequencies that have occurred we can determine the chelation sites. An absorption band around 3448 cm^{-1} cans be assigned to the stretching vibration band for the OH group υ(O–H) of COOH group. The stretching vibration of the C–H aromatic and C=N exhibited appeared at 3180–3152 cm^{-1} and 1601 cm^{-1}, respectively. The peaks appeared in the range of 1477–1458 cm^{-1} are assigned to the υ(C–C=C–C) bond. The difference value of 240–283 cm^{-1} between the asymmetric (1604–1561 cm^{-1}) and symmetric (1321 cm^{-1}) stretching vibration of the carboxylate group agrees with a monodentate type of chelation [23]. For free pia a band refers to stretching vibration of the C=O group is appeared at 1700 cm^{-1} which disappears in the Au(III) pia complex. The absorption peaks appeared at 755 cm^{-1} and 685 cm^{-1} for picolinic free ligand while these peaks are shifted to 702–763 cm^{-1} for the Au(III)–pia complex which can be assigned to deformation vibration of the pyridine ring and confirms that N atom of pyridine is chelated with Au(III) ion. The peaks appeared at 601, 559, 476 and 455 cm^{-1} are assigned to the stretching vibration bands of υ(Au–N) and υ(Au–O) [24]. The IR bands for isonicotinic acid (inta) free ligand appeared at 3550 and 1656 cm^{-1} referring to υ(O–H) and υ(C=O), respectively. For Au(III) inta complex this absorption band is absent due to chelation of Au(III) through the oxygen atoms of carboxylate group. This confirms that the coordination of inta occurs via the carboxyl oxygen to the Au(III) ion. The strong absorptions at 1563–1548 and 1419–1374 cm^{-1} come from the asymmetric (υ_{as}) and symmetric (υ_s) vibrations of the COO group. The $\Delta\nu$ ($\upsilon_{as} - \upsilon_s$) values are 144 cm^{-1}. The smaller $\Delta\nu$ value for the Au(III) inta complex indicates the bidentate character of isonicotinic acid. The absorption peaks appeared at 626 and 675 cm^{-1} and are assigned to the stretching vibration bands υ(Au–O) [24].

Table 2. Infrared frequencies (cm^{-1}) for Au(III) complexes.

Assignments	Compounds					
	nta	pia	inta	Au(III)–nta	Au(III)– pica	Au(III)–inta
ν_{as}(N-H); NH_2	3375	-	-	3420	-	-
ν_s(N-H); NH_2	3157	-	-	3150	-	-
ν(C=O)	1669	1700	1704	1702	-	-
ν(C=N)	1612	1601	1614	1600	1595	1610
ν(C-N)	1255	1260	1261	1205	1220	1244
ν_{as}(COO)	-	-	-	-	1604	1563
ν_s(COO)	-	-	-	-	1321	1419
Δν	-	-	-	-	283	144
ν(M–O)	-	-	-	-	660 645	675 626
ν(M–N)				603 545 460	601 559 476	-

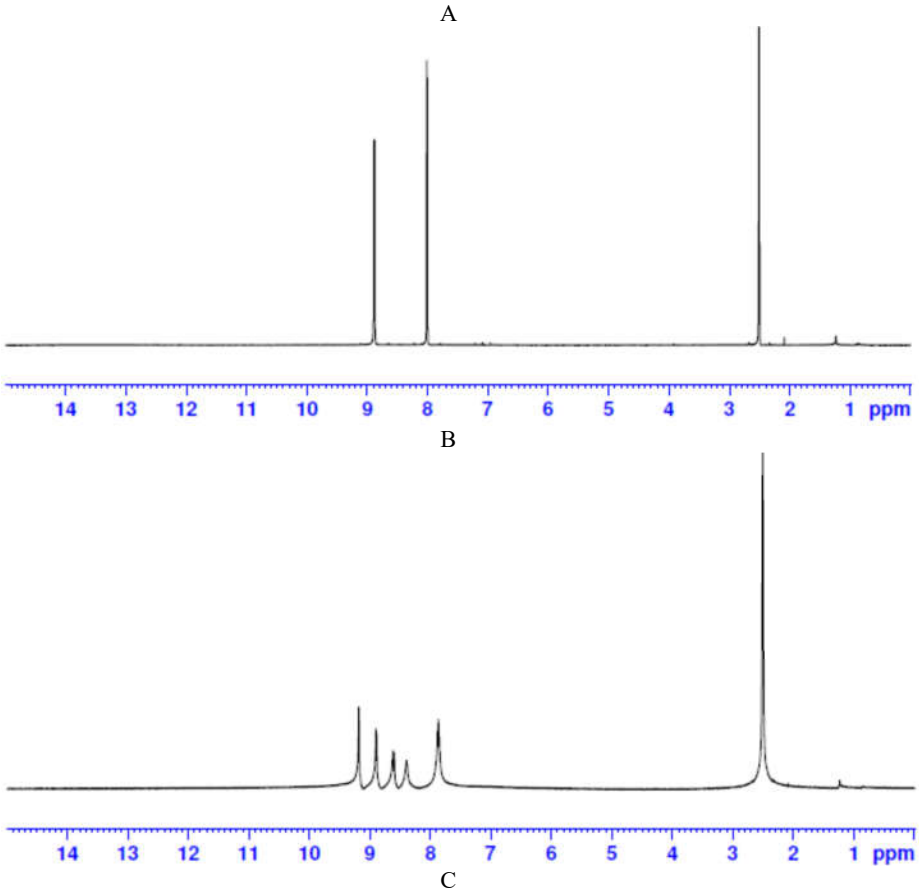
^{1}H-NMR spectra

^{1}H-NMR data for gold(III) complexes of nicotinamide, picolinic acid and isonicotinic acid are presented in Table 3 and displayed in Figure 3 as for free nicotinamide free ligand, ^{1}H-NMR spectrum has signals at δ: 9.08 (1H, C2-H), 8.25 (1H, C3-H), 7.53 (1H, C5-H), 8.74 (1H, C6-H) and (8.22 and 7.67) ppm (2H, NH_2). The picolinic acid ligand has signals at δ: 8.10 (1H, C2-H), 8.03 (1H, C4-H), 7.67 (1H, C5-H), 8.76 (1H, C6-H) and 11.18 ppm (1H, COOH). The isonicotinic acid ligand has signals at δ: 1.2 (1H, CH_3), 7.84 (1H, C3-H), 7.87 (1H, C4-H), 8.87 (1H, C5-H) and 9.17 (1H, C6-H). For Au(III) complexes and according to ^{1}H-NMR data, little chemical shifting is significant in the synthesised gold(III) complexes. These signals confirm the chelation of nicotinamide with Au(III) *via* N atom of pyridine [26], the chelation of picolinic acid with

Au(III) ion is occurred through O atoms of COOH group. Finally the chelation in case of isonicotinic acid with Au(III) ion through oxygen of carboxylic COOH group.

Table 3. ^{1}H-NMR spectral assignments of Au(III) complexes.

Signals	Au(III)–nta	Au(III)–pica	Au(III)–inta
[1H, C2-H]	8.888	8.11	9.17
[1H, C3-H]	8.87	--	8.89
[1H, C4-H]	--	8.12	7.87
[1H, C5-H]	7.99	7.72	8.38
[1H, C6-H]	8.884	8.75	--
H, NH_2	8.012 8.008	--	--
[1H, COOH]	--	--	--



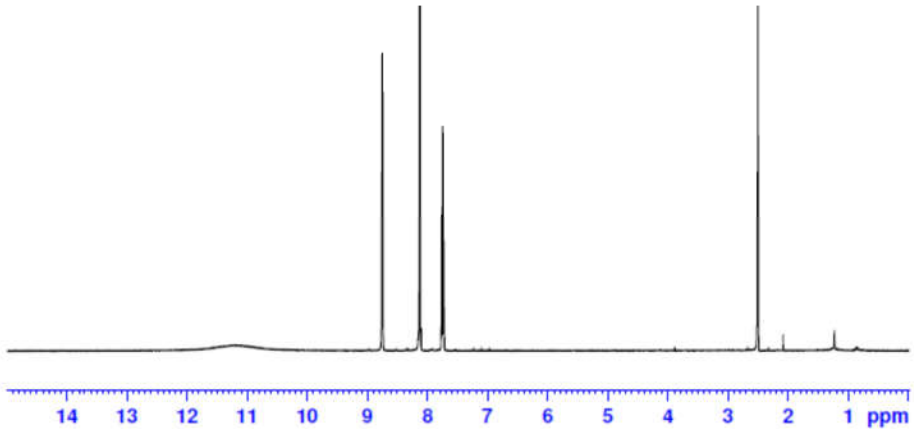


Figure 3. ^{1}H NMR spectra of (A): $[Au(nta)_2(Cl)_2].Cl$, (B): $[Au(pica)_2].Cl$ and (C): $[Au(inta)_2].Cl$ complexes.

Morphological analysis

Morphological analysis has a vital role for classifying the distinct formation of coordination compounds.

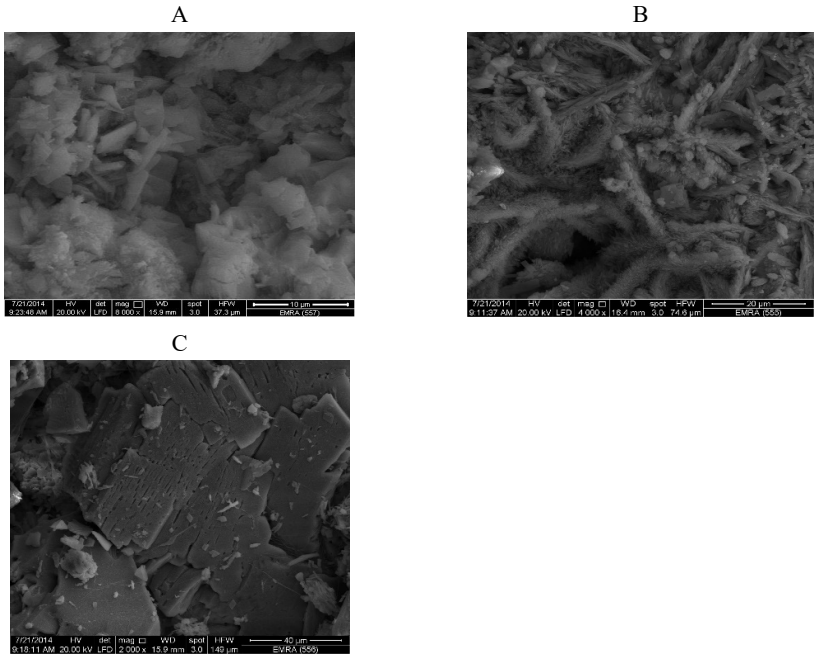


Figure 4. SEM images of (A): $[Au(nta)_2(Cl)_2].Cl$, (B): $[Au(pica)_2].Cl$ and (C): $[Au(inta)_2].Cl$ complexes.

From Figure 4, it is clear that the morphology of the Au(III) nicotinamide, Au(III) picolinic acid and Au(III) isonicotinic acid complexes show a homogenous distribution between Au(III) ion and chelating agents Figure 4. The surface morphology of Au(III) complexity were checked using SEM investigation which showed a small particles accompanied with high ability to agglomerate formation with different shapes in comparison with starting materials. The morphological properties of gold coordination compounds were characterized by XRD and TEM analysis.

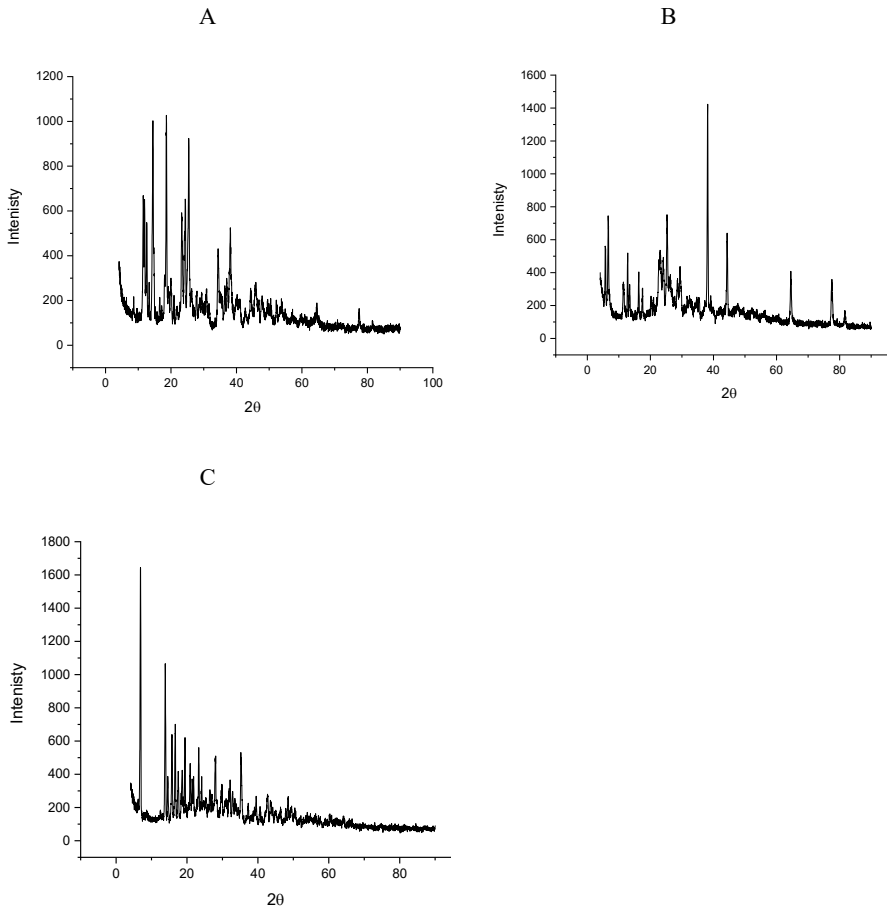


Figure 5. XRD spectra of (A): $[Au(nta)_2(Cl)_2].Cl$, (B): $[Au(pica)_2].Cl$ and (C): $[Au(inta)_2].Cl$ complexes.

The XRD diffractograms for Au(III) complexes are shown in Figure 5. The XRD analyses for all Au(III) complexes were occurred in solid state powder form. The XRD pattern showed sharp peaks, which might be due to the crystalline to semi crystalline behaviour. XRD patterns of the gold complexes consists of an important peak within the range of $2\theta = 2–90$. The particle size was calculated from the positions of intense peaks using Scherrer relationship [27]. Concerning Figure

5, the 2θ values with maximum intensity of the peaks for gold(III) complexes are observed at (10.36, 14.58, 20.20, 25.35, 28.16, 35.50 and 40.80), (7.66, 10.84, 12.55, 14.42, 17.65, 22.30, 24.63, 25.00, 28.26, 39.65, 42.50, 63.06,78.66 and 82.20) and (5.60, 15.17, 17.95, 19.22, 20.53, 22.50, 29.08 and 38.56) which corresponds to gold complexes of nicotinamide, picolinic acid and isonicotinic acid, respectively. This implies that Au(III) complexes have a nanostructure form within 20-50 nm.

TEM images of the synthesised gold complexes are exhibited in Figure 6. The complexes include spherical uniform nanoparticles with an average diameter within range 20-50 nm.

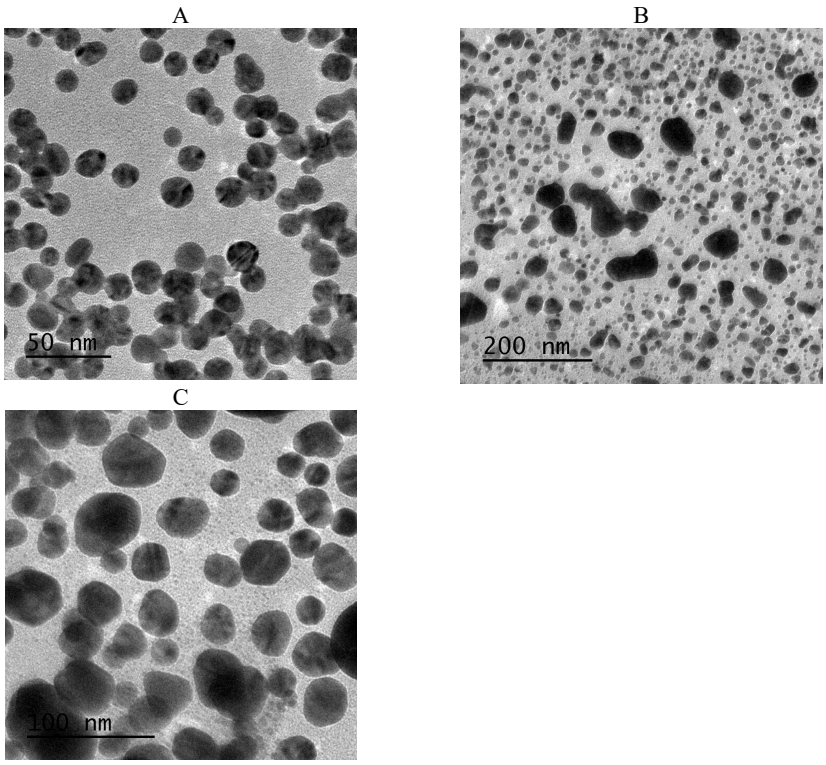


Figure 6. TEM images of (A): $[Au(nta)_2(Cl)_2].Cl$, (B): $[Au(pica)_2].Cl$ and (C): $[Au(inta)_2].Cl$ complexes.

CONCLUSION

Three newly gold(III) complexes $[Au(nta)_2(Cl)_2].Cl$, $[Au(pica)_2].Cl$ and $[Au(inta)_2].Cl$ were synthesized by reacting nicotinamide (nta), picolinic acid (pica), and isonicotinic acid (inta) with gold(III) chloride in ratio (gold : ligand) (1:2). The complexes were confirmed from FTIR, and ^1H NMR spectral analysis, morphological analysis (SEM, TEM, and XRD) and analytical data. The studies show that all gold(III) complexes have a four coordinated behavior. On the basis of the spectral studies show that the nicotinamide act as monodentate while both picolinic acid and isonicotinic acid acts as a bidentate chelate through the two oxygen atoms of carboxylate group.

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