Heteroatom Chemistry
Volume 16, Number 6, 2005

Synthesis, Characterization, and Antimicrobial Activities of Cu(I), Ag(I), Au(I), and Co(II) Complexes with $[CH_3N(CH_2PPh_2)_2]$

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Received 15 February 2005; revised 25 April 2005

ABSTRACT: *Transition metal complexes of ditertiary aminomethylphosphine ligand, $(Ph_2PCH_2)NCH_3$ [N,N-bis(diphenylphospinomethyl)aminomethane], dppam, with metal ions which are Ag(I), Au(I), Cu(I), and Co(II) have been synthesized under nitrogen atmosphere by the Schlenk method. $[Ag(dppam)_2]NO_3$ (**1**), $[Au(dppam)_2]Cl$ (**2**), and $[Cu(dppam)_2]Cl$ (**3**) complexes have been isolated as colorless solids, whereas $[CoCl_2(dppam)]$ (**4**) complex as a blue solid. All complexes have been characterized by atomic absorption, FT-IR, NMR (^1H, ^{13}C, ^{31}P) spectroscopic, thermogravimetric/differantial thermal analysis (TG/DTA), and elemental analysis techniques. Antimicrobial activity of* **1**, **2**, **3**, *and* **4** *were studied in vitro on 13 bacteria and 4 yeasts. The cobalt(II) phosphine complex has shown the best antimicrobial activity in comparison with the other metal complexes.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:484–491, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20145

INTRODUCTION

We have shown that a variety of functionalized chelating ditertiary aminomethylphosphines of the type $(R_2PCH_2)_2NR'$ can be obtained by treating the phosphonium salts $[R_2P(CH_2OH)_2]Cl$ with primary amines $R'NH_2$ [1–4].

The reported studies on antimicrobial and antitumoral activities of Ag(I) and Au(I) complexes using phosphines show a wide spectrum of antimicrobial activities [5,6]. It has also been reported that Au(I) bis(diphosphine) complexes such as $[Au(dppe)_2]^+$ (dppe = 1, 2-diphenylphosphinoethane) and optically active phosphine-gold(I) complexes are active against some types of cancer [7].

In spite of the researches on the chemistry and catalytic activities of metal–phosphine complexes, the biochemistry of aminomethylphosphines having P–C–N linkage has not been studied extensively so far. Therefore, our interest in aminomethylphospines has prompted us to synthesize novel aminomethylphosphine–metal complexes of Au(I), Ag(I), Cu(I), and Co(II) and to explore some biological properties of these complexes.

EXPERIMENTAL

Materials and Chemical Reagents

Chemistry. The metal contents of the complexes were measured by atomic absorption spectroscopy on Hitachi 180-80 polarized Zeiman atomic absorption spectrometer. Elemental analysis was performed with LECO CHNS 932. Melting points

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Contract grant sponsor: Çukurova University Research Fund.

were determined in open capillary tubes on digital Gallenkamp melting point apparatus and are uncorrected. FT-IR spectra were obtained using KBr pellets with Perkin-Elmer RX1 FT-IR system in the range 4000–450 cm^{-1}. ^{1}H-NMR, ^{13}C, and ^{31}P-NMR spectra were recorded at 25°C in DMSO-d^6 and $CDCl_3$ on a Varian mercury 200 MHz NMR spectrometer. $^{31}P\{^{1}H\}$-NMR spectra were measured with reference to an external standard 85% H_3PO_4 in H_2O. Thermogravimetric and differential thermal analysis (TG/DTA) were acquired using a Pyris diamond TG/DTA Perkin-Elmer thermal analysis and Pyris 7.0 data-processing system. TG/DTA measurements were run under nitrogen atmosphere with a temperature ramp of 20°C min^{-1} between 25–700°C. All chemicals and solvents were purchased from Merck, Aldrich, Sigma, Fluka, and Riedel-de Haën and used without further purification. All reactions were carried out under nitrogen atmosphere using the Schlenk technique.

Bioassay. Antimicrobial activities of the metal complexes were determined using the agar-disc diffusion method [8]. These microorganisms were provided by the Microbiology Laboratory Culture Collection, Department of Biology, Sütçü İmam University, Turkey. The test materials were purified and dried as much as possible. The bacteria were first incubated at 37 ± 0.1°C for 24 h in nutrient broth (Difco), and the yeasts were incubated in Sabourand dextrose broth (Difco) at 25 ± 0.1°C for 24 h. After injecting 0.1 mL cultures of the bacteria and yeast (prepared as above) into petri dishes (9 cm) (10^7/ for the bacteria and 10^6/ for the fungi), 15 mL of Mueller Hinton agar (MHA, Oxoid) and Sabourand dextrose agar (SDA) (sterilized in a flask and cooled to 45–50°C) were homogeneously distributed onto the sterilized petri dishes [9,10]. Sterilized blank paper discs 6 mm in diameter (Schleicher & Schüll no: 2668, Germany) were saturated with 800, 1000, and 1200 μg of chemical samples per disc, then placed onto the agar plates which had previously been inoculated with the above organisms [10,11]. The discs injected only with DMSO were used as control. Blank paper discs treated with ampicillin, streptomycin, and nystatin-saturated antibiotics (Eczacıbaşı İlaç Sanayi, Turkey) were used as positive controls. After the plates combined with the discs were left at 4°C for 2 h, the plates injected with yeast were incubated at 25 ± 0.1°C for 24 h and those injected with bacteria were incubated at 37 ± 0.1°C for 24 h [11–13]. At that time, inhibition zones appearing around the discs were measured and recorded in millimeter.

Synthesis

$CH_3N(CH_2PPh_2)_2$ (dppam). The phosphonium salt, $[PPh_2(CH_2OH)_2]Cl$, and dppam ligand were prepared according to [3,4,14]. 1.0 mL Triethylamine (99%) added to a stirred solution of $[PPh_2(CH_2OH)_2]Cl$ (1 g, 3.5 mmol) in 30 mL ethanol (2:1, EtOH:water). 1.8 mL Methylamine (40%) was syringed into the cloudy solution, and the mixture was refluxed for 1 h. After cooling, the oily product was extracted with dichloromethane and dried over Na_2SO_4.

*$[Ag(dppam)_2]NO_3$ (**1**)*. 0.243 g (0.568 mmol) dppam was added in the Schlenk tube having 10 mL dichloromethane, and 0.048 g (0.284 mmol) $AgNO_3$ dissolved in 10 mL ethanol was poured slowly into dppam solution while stirring. The tube was wrapped with a folio to protect it from light, and the mixture was stirred for 2 h. While the solvent volume was reduced, the white solid started to precipitate and with the addition of diethyl ether completed the precipitation. The white solid was filtered off and washed with diethyl ether several times and dried in vacuo. The product is soluble in $CHCl_3$, CH_2Cl_2, DMSO and insoluble in water, ethanol, petroleum ether, and diethyl ether. mp 240.3°C (decomp.). Yield: 0.180 g (62%). Anal. calcd for $AgC_{54}H_{54}N_3P_4O_3$ or $[Ag(dppam)_2]NO_3$: C, 63.29; H, 5.31; N, 4.10; Ag, 10.52. Found: C, 63.01; H, 5.19; N, 4.05; Ag, 10.02 (AAS result). *TG/DTA data* : No weight loss was observed below decomposition temperature; decomposition began at 238.11°C and three endothermic peaks were at around 257.34, 450.27, and 582.78°C. FT-IR (KBr) : ν 3058–3049 (m, Ar-H); 2972–2768 (m, R-H); 1952, 1894, 1816 (w, monosubstitute Ar-H); 1582 (w, C=C (Ph)), 1484 (m, C—H); 1434 (s, C=C (Ph)); 1408, 1384 (w, CH_3-N); 1156–1040 (m, C—N (ter-amine)); 750–694 (s, monosubstitute Ar-H); 522–486 (w, P-Ph_2) cm^{-1}. ^{1}H-NMR (DMSO-d^6, 25°C): δ 7.533–7.024 [m, 40H, 8Ph], 3.584 [d, $^{2}J_{HH}$ = 8.6 Hz, 8H, 4 (P-C$\underline{H}_2$-N)], 2.362 [s, 6H, 2(N-C$\underline{H}_3$)] ppm. ^{13}C-NMR (DMSO-d^6, 25°C): δ 133.696–128.99 [m, Ph], 58.113 [br, P-$\underline{C}H_2$-N], 38.093 [s, N-CH_3] ppm. ^{31}P-NMR (DMSO-d^6, 25°C): δ 36.276 [br, Ag-$\underline{P}Ph_2$] ppm.

*$[Au(dppam)_2]Cl$ (**2**)*. 1.44 g (3.366 mmol) dppam was added in the Schlenk tube having 10 mL dichloromethane and treated with 0.223 g (0.561 mmol) $NaAuCl_4{\cdot}2H_2O$ dissolved in ethanol. The mixture was refluxed for 15 min and then stirred for 2 h at room temperature. The yellow mixture gradually became colorless. The volume of the mixture was reduced, addition of diethyl ether completed precipitation, and the white solid product was filtered off, washed with diethyl ether several times, and dried in vacuo. The product is soluble in $CHCl_3$, CH_2Cl_2, DMSO, and

insoluble in water, ethanol, petroleum ether, and diethyl ether solvents. mp 195.6°C (decomp.). Yield: 0.5493 g (90%). Anal. calcd for $AuC_{54}H_{54}N_2P_4Cl$: C, 59.65; H, 5.02; N, 2.58; Au, 18.11. Found: C, 59.03; H, 4.99; N, 2.05; Au, 17.26 (AAS result). *TG/DTA data* : no weight loss was observed below decomposition temperature; decomposition began at 199.85°C, and three endothermic peaks were at around 248, 302, and 342°C. FT-IR (KBr) : ν 3124–3046 (m, Ar-H); 2916–2784 (s, R-H); 1956, 1880, 1804 (w, monosubstitute Ar-H); 1582, 1568 (w, C=C (Ph)), 1474 (m, C—H); 1434 (s, C=C (Ph)); 1384, 1274 (w, CH_3-N); 1094 (m, C—N (ter-amine)); 738–692 (s, monosubstitute Ar-H); 534–484 (w, P-Ph_2) cm^{-1}. ^{1}H-NMR (DMSO-d^6 + $CDCl_3$, 25°C): δ 7.135–6.711 [m, 40H, 8Ph], 3.28 [br, 8H, 4 (P-CH_2-N)], 2.193 [s, 6H, 2 (N-CH_3)] ppm. ^{13}C-NMR (DMSO-d^6 + $CDCl_3$, 25°C): δ 132.793–128.006 [m, Ph], 61.992 [s, P-$\underline{C}H_2$-N], 38.163 [s, N-CH_3] ppm. ^{31}P-NMR (DMSO-d^6, 25°C): δ 52.941 [s, Au-$\underline{P}Ph_2$] ppm.

*[Cu(dppam)$_2$]Cl (**3**)*. 1.161 g (3.768 mmol) dppam was dissolved in the Schlenk tube using 10 mL dichloromethane. 0.0957 g (0.628 mmol) $CuCl_2 \cdot 2H_2O$ dissolved in 10 mL ethanol was poured slowly into dppam solution while stirring. The blue color of copper(II) solution gradually became colorless. Having reduced the volume of solution and added diethyl ether, the solid was obtained which was filtered off, washed, with diethyl ether several times and dried in vacuo. The product is soluble in $CHCl_3$, CH_2Cl_2, DMSO, and insoluble in water, ethanol, petroleum ether, and diethyl ether mp 160.9°C. Yield: 0.485 g (81%). Anal. calcd for $CuC_{54}H_{54}N_2P_4Cl$: C, 67.99; H, 5.71; N, 2.94; Cu, 6.66. Found: C, 67.11; H, 5.19; N, 2.90; Cu, 6.10 (AAS result). *TG/DTA data*: no weight loss was observed below decomposition temperature; decomposition began at 176.2°C, and three endothermic peaks were at around 232.97, 336.86, and 580.05°C. FT-IR (KBr) : ν 3064–3053 (m, Ar-H); 2940–2788 (s, R-H); 1956, 1888, 1812 (w, monosubstitute Ar-H); 1584 (w, C=C (Ph)), 1482 (m, C—H); 1434 (s, C=C (Ph)); 1408 (w, CH_3-N); 1094 (m, C—N (ter-amine)); 740–696 (s, monosubstitute Ar-H); 552–488 (w, Cu-PPh_2) cm^{-1}. ^{1}H-NMR (DMSO-d^6, 25°C): δ 7.492–7.146 [m, 40H, 8Ph], 3.832 [d-br, 8H, 4 (P-$C\underline{H}_2$-N)], 2.050 [s, 6H, 2 (N-$C\underline{H}_3$)]] ppm. ^{13}C-NMR (DMSO-d^6, 25°C): δ 133.211–128.7 [m, phenyl], 59.274 [br, P-$\underline{C}H_2$-N], 30.590 [s, N-$\underline{C}H_3$] ppm. ^{31}P-NMR (DMSO-d^6, 25°C): δ 50.965 [s, Cu-$\underline{P}Ph_2$] ppm.

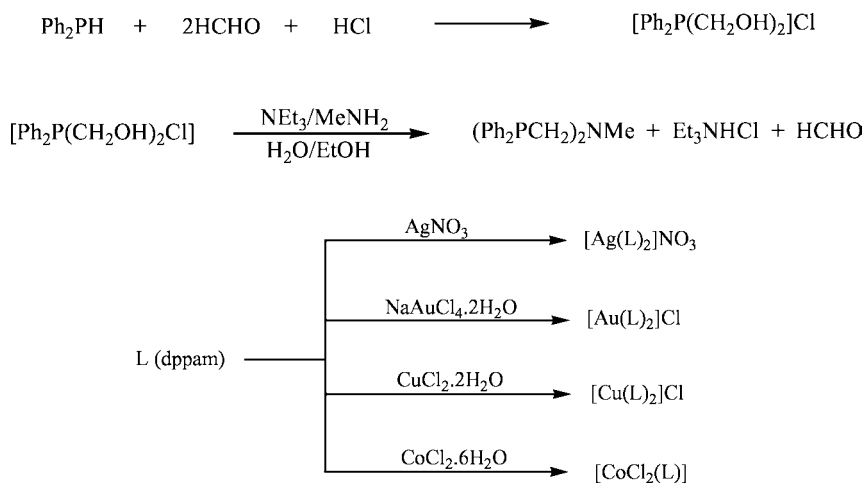
*[$CoCl_2$(dppam)] (**4**)*. 0.121 g (0.283 mmol) dppam was added into the Schlenk tube having 10 mL dichloromethane. 0.0775 g (0.283 mmol) $CoCl_2 \cdot 6H_2O$ dissolved in 10 mL ethanol was poured slowly into dppam solution while stirring. During the reaction, the initial dark red color of cobalt(II) solution gradually turned into blue after stirring of 15 min. After reducing the volume of the mixture, the blue solid was obtained from the solution and precipitation was completed with addition of diethyl ether. The product was filtered off, washed with diethyl ether, and dried in vacuo. The solid is soluble in $CHCl_3$, CH_2Cl_2, DMSO solvents, and insoluble in water, ethanol, petroleum ether, and diethyl ether. mp 105.9°C. Yield: 0.134 g (85%). Anal. calcd For $CoC_{27}H_{27}NP_2Cl_2$: C, 58.19; H, 4.88; N, 2.52; Co, 10.57. Found: C, 58.08; H, 4.03; N, 2.12; Co, 10.01 (AAS result). *TG/DTA data*: no weight loss was observed below decomposition temperature; decomposition began at 123.22°C and three endothermic peaks at around 153.59, 292.73, and 549.54°C. FT-IR (KBr) : ν 3054 (m, Ar-H); 2940–2788 (s, R-H); 1960, 1894, 1814 (w, monosubstitute Ar-H); 1588 (w, C=C (Ph)), 1482 (m, C—H); 1437 (s, C=C (Ph)); 1324–1274 (w, CH_3-N); 1140–1026 (m, C—N (ter-amine)); 742–692 (s, monosubstitute Ar-H); 568–510 (w, Co-PPh_2) cm^{-1}. ^{1}H-NMR (DMSO-d^6, 25°C): δ 7.675–7.211 [m, 20H, 4Ph], 3.617 [br, 4H, 2C$\underline{H}_2$-N], 2.420 [br-s, 3H, N-C$\underline{H}_3$] ppm. ^{13}C-NMR (DMSO-d^6, 25°C): δ 130.411–125.822 [m, Ph], 59.6 [br, P-CH_2-N], 28.5 [s, N-CH_3] ppm. ^{31}P-NMR (DMSO-d^6, 25°C): δ 51.877 [s, Co-$\underline{P}Ph_2$] ppm.

RESULTS AND DISCUSSION

Synthesis

Dppam ligand was synthesized by treating phosphonium salt with primary amines according to the Mannich reaction, and the transition metal complexes of the aminomethylphosphine ligand were prepared under nitrogen atmosphere using Schlenk techniques as shown in Scheme 1 [1].

The metal complexes **1**,**2**,**3**, and **4** were obtained by the reaction of dppam in CH_2Cl_2 with appropriate amount of metal salts dissolved in absolute ethanol, respectively. Since the metal–aminomethylphosphine complexes are insoluble in diethyl ether, the products can easily be separated from the mixture with the addition of diethyl ether. Due to the fact that aminomethylphosphines can easily be oxidized, Au(III) and Cu(II) ions were reduced to Au(I) and Cu(I) during the reaction by using excess dppam ligand in synthesis of the complexes **2** and **3**. The reduction of Au(III) to Au(I) and Cu(II) to Cu(I) was monitored with color changes from yellow to colorless and from blue to colorless, respectively, as expected. Even though the solid state of the complexes are stable in air, they all can decompose in a solution having small quantity of water and oxygen.



SCHEME 1

Characterization

In order to characterize the metal complexes, AAS, FT-IR, NMR, TG/DTA, and elemental analysis techniques were used.

The examination of ^{1}H-NMR spectra of the complexes showed that the aromatic protons of the phenyl ring substituted on phosphorus have the chemical shift value (δ) in a range of 6.8–7.6 ppm. The characteristic P-CH_2-N protons and N-CH_3 protons of aminomethyl phoshines of the metal complexes are observed around 3.6 ppm and 2.2 ppm, respectively which are consistent with those of reported data [1–4].

^{31}P-NMR spectra of the complexes showed more shielded signals compared with the free aminomethylphosphine ligand observed at −27.53 ppm according to the literature [3]. Table 1 shows the coordination shift (δ) of the complexes along with the chemical shifts of the complexes. The coordination shift values of the complexes (Δ), which can be defined by $\Delta = \delta$ (complex) $- \delta$ (free ligand), vary depending on the metal centers and the ligand itself. The values of Δ have been correlated to many metal phosphine complexes [13]. The specific ^{31}P-{^{1}H} NMR peaks of the complexes have been observed at 36.276 (br), 52.941 (s), 50.965(s), and 51.877(s) ppm for **1**, **2**, **3**, and **4**, respectively. These chemical shifts prove that the complexes were obtained as expected, in comparison with the literature [14–28]. The silver(I) complex is expected to show Ag coupling to P nuclei. However, the solution NMR has shown a broad peak of P atoms at room temperature.

The metal aminomethylphosphine complexes were further characterized by FT-IR spectra. Table 1 also presents the FT-IR data of the complexes which show C–N–C stretching peaks around 1150–1040 cm^{-1} for tertiary amine. Aromatic C-H stretching band has been found at about 3058–3042 cm^{-1}; the peaks around 1816–1952 cm^{-1} and 694–750 cm^{-1} are assigned for monosubstitute benzene whereas bands in the range of 2940–2780 cm^{-1} are for aliphatic C-H stretching [14,28]

Elemental analysis for C, H, N and atomic absorption spectroscopy for metal contents show the basic formulas of the complexes. Based on the spectral and analytical data, metal to ligand ratio has been found as 1:2 for the complexes **1**, **2**, and **3** and 1:1 for the complex **4**. Because of the fact that we could not obtain suitable crystals of the synthesized complexes for further structural characterization with single crystal X-ray crystallography, we evaluated the structures of the complexes by using sufficient analytical and spectroscopic data. Since metal ions of Ag(I), Au(I), and Cu(I) are diamagnetic, their expected geometry is distorted tetrahedral whereas paramagnetic Co(II) complex is expected to be as square planar. Computer drawing of complex **1**, **2**, **3** on Chem Draw 3D based on analytical data showed tetrahedral geometry of metal center having P–M–P bond angles consistent with those of reported tetrahedral Au(I), Ag(I), Cu(I) complexes as shown Fig. 1 [6,24,29,30].

Ionic structures of **1**, **2**, **3**, and **4** complexes were tested with simple qualitative tests. According to the results of these tests, Cl^{-} ions are not in coordination sphere for **1**, **2**, and **3**, whereas Cl^{-} ions have coordinated to Co(II) for the complex **4**.

All complexes have shown three endothermic peaks in TG/DTA results. Ag(I) complex was stable at the temperature of 238.11°C, and decomposition started at this temperature and was completed

TABLE 1 ^{31}P-NMR Chemical Shifts (ppm), Selected FT-IR Peaks (cm^{-1}), Elemental Analysis and Atomic Absorption, and TG/DTA Results of the Complexes

Complexes	*Molecular Weight (Yield %)*	*^{31}P-NMR (δ, ppm) Coordination Shifts (Δ)*	*FT-IR (cm^{-1})*	*Elemental Analysis Found (%) Analytical Calcd (%)*			*Atomic Absorption Found (%) Analytical Calcd (%)*	*Endothermic Peaks (°C)*
1	1024.808	36.276 (d-br)	1408, 1384 (CH_3-N); 1156,1040 (C-N);	63.01	5.19	4.05	10.02	257.34, 450.27, 582.78
	(62)	(63.806)	522–486 (P-Ph_2)	63.29	5.31	4.10	10.52	
2	1087.356	52.941 (s)	1302,1274 (CH_3-N); 1094(C-N);	59.03	4.99	2.05	17.26	248, 302, 342
	(90.2)	(80.471)	534–484 (P-Ph_2)	59.65	5.01	2.58	18.11	
3	953.935	50.965 (s)	1408(CH_3-N); 1094 (C-N);	67.11	5.19	2.90	6.10	232.97, 336.86, 580.05
	(81)	(78.495)	552–488 (P-Ph_2)	67.99	5.71	2.94	6.66	
4	557.327	51.877 (s)	1302,1274 (CH_3-N); 1156,1040 (C-N);	58.01	4.03	2.12	10.01	153.59, 292.73, 549.54
	(85)	(79.407)	568–510 (P-Ph_2)	58.19	4.88	2.52	10.57	

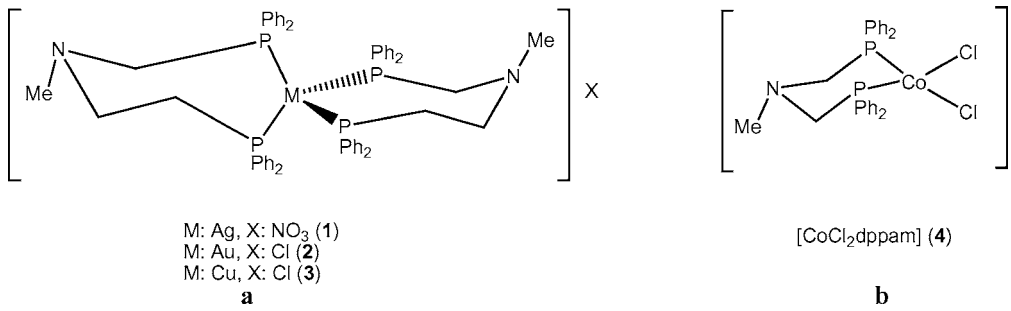


FIGURE 1 Tetrahedral Au(I), Ag(I), Cu(I) complexes (a) and square planar Co(II) complex (b).

at 280°C. The second endothermic peak began at 433.86°C and finished at 471.85°C. The last endothermic peak was between 569.72°C and 601.86°C.

The decomposition of the complex of Au(I) began at 179.85°C and continued to 265°C. Other two endothermic peaks were respectively between 299.7–319.5°C and 325.8–405.9°C.

Cu(I) complex decomposed at the temperature of 176.2°C, and the first endothermic step finished at 249.54°C. The second step of decomposition was at 250.01–470.81°C when a great deal of mass was removed. The last peak started at the temperature of 573.22°C and completed at the temperature of 590.93°C.

The endothermic peaks of Co(II) were around 123.22–177.02°C, 182.09–291.72°C, and 544.47–559.7°C.

Antimicrobial Activity

Growth inhibitory activity of the chemical materials was tested against 13 bacteria (e.g., *Corynebacterium xerosis* UC9165, *Bacillus brevis* FMC 3, *Bacillus megaterium* DSM 32, *Bacillus subtilis* IMG 22, *Mycobacterium smegmatis* RUT, *Pseudomonas aeruginosa* DSM 50071, *Staphylococcus aureus* Cowan 1, *Klebsiella pneumoniae* FMC 5, *Klebsiella oxytocica* A, *Enterococcus faecalis* CR 25, *Micrococcus luteus* LA 2971, *Escherichia coli* ATCC 25922, and *Yersinia enterocolitica* CR 38) and four fungi (*Kluyveromyces fragilis, Rhodotorula rubra, Saccharomyces cerevisiae* WET 136, and *Candida albicans*). The homogeneous solutions of the complexes were prepared in DMSO which showed no activity as a solvent in these assays. Compounds were initially dissolved in DMSO in the minimal volume, then serially diluted with media to the concentration, so there was very minimal residual DMSO in the assayed medium.

Investigation of the antimicrobial activity of the complexes showed almost similar results except for complex **4**. As given in Table 2, Cu(I), Ag(I), and Au(I) complexes have been found inactive at the concentration of 800 μg/disc and 1000 μg/disc against tested bacteria and fungi respectively, whereas the Co(II) phosphine complex (**4)** has shown moderate activity at 1000 μg/disc. The compounds **1,2**, and **3** are moderately active at the concentration 1200 μg/disc; however, the compound **4** showed the best activity when compared with **1**, **2**, and **3**. Cobalt complex has almost shown similar activity against some of the bacteria when compared with the standard antibiotics like ampicillin and streptomycin. Activity of cobalt complex against some fungi has been measured and is very close in nystatin (an antifungal).

The results are useful to explaining the dppam complexes of Ag(I), Au(I), Cu(I) which are thought of as inert complexes in terms of microbiological activities, whereas Co(II) complex shows labile property. This differentiation could be explained as due to having less bulky geometry of the square planar Co(II) complex. The structural characterization showed that complexes **1, 2**, and **3** with bidentate tertiary aminomethylphosphine ligand, dppam, are sterically crowded more than the complex **4**. Therefore, the microbiological activity of the compound **4** is different from **1**, **2**, and **3**.

CONCLUSIONS

The complexes Ag(I), Au(I), Cu(I), and Co(II) with bidentate tertiary aminomethylphosphine ligand (dppam) have been synthesized and characterized by using spectroscopic, thermal, and microanalytical methods. ^{31}P-{^{1}H}NMR spectra of the metal complexes have indicated that coordination of aminomethylphosphine ligand to metal center gives deshielded chemical shift value compared with free ligand.

Antimicrobial activities of the metal complexes were determined using the agar-disc diffusion method. Ampicillin, streptomycin, and nystatin-saturated antibiotics were used as positive controls.

TABLE 2 Antimicrobial Activities of **1, 2, 3**, and **4** and Antibiotics for Positive Control

	Inhibition Zone (mm)										
	1000 μg Complex/disc				*1200 μg Complex/disc*				*Standard Antibiotics*		
Microorganisms	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	*A10*	*S10*	*N30*
Corynebacterium xerosis	–	–	–	–	9	10	7	7	12	10	–
Bacillus brevis	–	–	–	7	8	7	7	12	14	16	–
Bacillus megaterium	–	–	–	11	7	7	–	19	11	17	–
Bacillus subtilis	–	–	–	10	8	8	7	15	15	18	–
Mycobacterium smegmatis	–	–	–	8	9	7	7	12	19	15	–
Pseudomonas aeruginosa	–	–	–	10	8	8	7	15	10	13	–
Staphylococcus aureus	–	–	–	8	8	7	10	13	16	21	–
Klebsiella pneumoniae	–	–	–	7	7	9	8	11	17	16	–
Klebsiella oxytocica	–	–	–	7	8	8	7	12	15	14	–
Enterococcus faecalis	–	–	–	16	–	7	–	20	16	17	–
Micrococcus luteus	–	–	–	8	7	7	10	12	33	–	–
Escherichia coli	–	–	–	8	8	8	–	14	11	–	–
Yersinia enterocolitica	–	–	–	7	7	7	7	11	13	17	–
Kluyveromyces fragilis	–	–	–	–	10	7	9	7	–	–	15
Rhodotorula rubra	–	–	–		9	7	8	8	–	–	14
Saccharomyces cerevisiae	–	–	–	10	9	8	–	16	–	–	18
Candida albicans	–	–	–	7	–	7	–	12	–	–	16

Standard antibiotic discs; A10: ampicillin (10 μg/disc); S10: streptomycin (10 μg/disc); N30: nystatin (antifungal, 30 μg/disc).

At concentrations of 800 μg/disc and 1000 μg/disc, the complexes **1–3** are inactive against tested bacteria and fungi, whereas the compound **4** is more active than others. The compounds **1, 2**, and **3** have shown moderate activity at the concentration of 1200 μg/disc; however, the compound **4** has shown the best activity when compared with **1, 2**, and **3** and similar activity as those of antibiotics.

ACKNOWLEDGMENTS

We would like to thank Prof. Dr. Yaşar Gök and Miraç Nedim Mısır for NMR measurements. The authors also are thankful Research Fund of Çukurova University for financial support to this project.

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