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Preparation Some Complexes of transition and non-transition metals and try to Using as Dental Restorative

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ABSTRACT

The work present in this study deals with preparation and characterization of new complexes which contain some transition ions (Sc^{3+}, Ti^{3+}, V^{5+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) and non-transition metal ions (Ba^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, and Sn^{2+}) with ligands (Thymol, Vanillin, o,m,p-Cresol, Salicylic acid, Methyl salicylate, Guaiacol, Eugenol, and Menthol). The prepared complexes were classified in accordance with the nature of the ligand (mondentate or bidentate) and the valance state of the metal ion, this giving the general formula; $[ML_2]$, $[ML_2.\ n\ H_2O]$ and $[ML_3]$. The prepared complexes have been characterized by elemental analysis, molar conductance, infrared and UV-Visible spectra and magnetic susceptibility measurement. The measurement of conductivity in chloroform indicate that all the complexes act as non-electrolyte- irrespective of the metal salt used in preparation , the magnetic and spectral measurement assigned the complexes with different geometrical structure viz., tetrahedral, square planar, or octahedral structure. The prepared complexes subsequently tried as dental filling passing the required tests of color, pH, setting time, consistency, compressive strength, film thickness, microlekage, and antibacterial. The complex [calcium-guaiacolate] show superiority in this respect and it is hoped that this complex (as dental filling) establish a chemical binding with the calcium of the tooth.

INTRODUCTION

Dental chemistry: Chemistry is important in several aspects of dentistry. Foremost is the structure of tooth enamel, the chemical reactions of breakdown and reformation of the enamel, and the role of fluoride in prevention of decay. Chemistry is also involved when the dentist enters the picture (1-6).

Dental Cement: Dental cements are materials of comparatively low strength, but they are used extensively in dentistry when strength is not a prime consideration. With two possible exceptions, they are not truly adhesive to enamel and dentin. Except for the resin cement they dissolve and erode in oral fluids. Such defects are likely to make them impermanent. However, regardless of certain inferior properties, they possess so many desirable characteristic that they are used in 40 to 60 per cent of all restoration. They are employed as (1) cementing (referred to as luting) agents for fixed cast restorations or orthodontic bands, (2) as thermal insulators under metallic restorations, (3) for temporary or permanent restorations, (4) as root canal sealant, and (5) as pulp capping agents. It should be reemphasized that as a group their chemical and physical properties leave much to be desired, and the manipulative techniques be designed to provide the optimal behavior (7).

Acid –Base reaction cements

Chief constituents: Dental cements are formulated as powders and liquids. The powders are amphoteric or basic (proton acceptors) and the liquids are acids or proton donors. On mixing the two together a viscous paste is formed, which subsequently hardens to a solid mass. The cements can be classified by the nature of the cement powder.

(a) Zinc oxide. This can react with a range of liquids.

(b) Ion-leachable glasses, particularly fluorine containing aluminosilicate(8).

General reactions: A cement forming reaction is the interaction between an acid and a base, the product of which is a gel-salt. Equations for such reactions can be written in a simplified general form: (8)

$$\underset{\text{Proton Acceptor}}{MO} + \underset{\text{Proton donor}}{H_2A} \longrightarrow \underset{\text{gel-salt}}{MA} + H_2O$$

$$\underset{\text{Proton Acceptor}}{MO \times SiO_2} + \underset{\text{proton donor}}{H_2A} \longrightarrow \underset{\text{gel-salt}}{MA} + x\,SiO_2 + H_2O$$

Set cement are heterogeneous, only part of the reacts with the liquids, and the final set material is composed of a core of unreacted powder surrounded by a matrix of reaction products, i.e. the gel-salt.

Zinc oxide–eugenol (ZOE) and non-eugenol cements

When certain types of zinc oxide are mixed with eugenol, the mix sets to hard cement that in suitable formulations is compatible with both the hard and soft tissues of the mouth. Cements of this type have been used extensively in dentistry since 1890$_s$. Simple mixture of these two materials did not have great strength when compared with the zinc phosphate cements, and their use in dentistry was limited for many years to situations in which strength was not important. Quite early in their use it was found that they had a sedative effect on exposed dentin and that they made an excellent temporary restoration. For many years the cements were used as temporary restorations, as soft tissue packs in oral surgery and periodontics, and as root canal sealers. Recently, non-eugenol-zinc oxide cements for temporary cementation has become available. These cements are suitable for patients sensitive to eugenol (7,9,10,11).

Chemistry of setting: Zinc oxide can react with eugenol to give a chelate, zinc eugenolate. This reaction is important in zinc oxide eugenol cements and impression materials. (8): This study was undertaken to prepare complexes of certain compounds (ligands) that can be used as dental temporary filling. Ten compounds were selected to mix with fourteen transitions and non- transition elements.
The objective of this study is to evaluate the new prepared materials, according to chemical, physical, dental measurements in ADA (American Dental Association) specification No.8, and the results were compared with those obtained from the standard (Zinc oxide-eugenol cement) which was used in this research as a control. The following tests were used to study the prepared fillings: (pH) measurements, Setting time, Compressive strength, Film thickness, Solubility of the complexes, Consistency of the complexes, Antibacterial effect and Microlekage of the complexes.

EXPERIMENTAL

The ligands that used in the study (Thymol, salicylic acid, menthol, ortho, meta, para- cresol, methyl salicylate and vanillin (Fluka company), and Eugenol from dori Dent, Dr-Hirschberg, Wien, Austria, were of analar grade and were used without further purification. $TiCl_3$ was prepared by refluxing titanium metal with concentrated hydrochloric acid until the solution changes to violet color (12). $ScCl_3$ was prepared by refluxing scandium oxide (Sc_2O_3) with concentrated hydrochloric acid until complete dissolution.

Preparation of complexes: The ligands were checked by their melting point and infrared spectroscopy. The complexes were prepared by the following methods: **First**: 2 mmole of the ligand salt (R^-Na^+) (R= eugenol, salicylic acid, thymol, vanillin, methyl salicylate, o-m-p-cresol, guaiacol, and menthol) were dissolved in 25 ml distilled water at room temperature. The resulting clear solution added to selected element salt [$BaCl_2$, $CaCl_2$, $Ca(CH_3COO)_2$, $ScCl_3$, $TiCl_3$,$VoCl_3$, $CrCl_3$, $MnCl_2.4H_2O$, $Mn(CH_3COO)_2.2H_2O$, $FeCl_3$, $CoCl_2.6H_2O$, $Co(CH_3COO)_2$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $Cu(CH_3COO)_2$, $ZnCl_2$, $Zn(CH_3COO)_2$, $Cd(CH_3COO)_2$, $SnCl_2$] dissolved in 5 ml distilled water . The colored solution started to deposit crystalline product almost immediately. The mixture was left for one hour and the crystals were filtered off, washed several times with small portions of warm water and dried in vacuum for several hours. The yield is almost quantitative.

Second: The phenol oil and element oxide or acetate were mixed with spatula in slab at room temperature until a uniform paste or a solidified complex, is obtained. All the prepared complexes were characterized by Infrared spectra, Uv-visible spectra and elemental analysis. The pH measurements were carried out with a Corning pH measuring apparatus (pH 105). All experimental solutions for pH measurements were done in distilled water. All the ligands and metals complexes with their colors products were listed in (Table 6).

Preparation of cements: The prepared complexes were based on several criteria with involving suitable color (pink or white), neutral pH or alkaline but not acidic, toxicity of metal. In addition the selection of ligand was based on toxicity and irritant to the common dentist uses, accordingly CaO was selected as ideal to be mixed with ligands (eugenol (E), guaiacol (G), and methyl salicylate (M)), the perfect formula was 70% calcium oxide and 30% rosin without any accelerator or retarder. The powder of temporary filling prepared was passed through the sieve with 150 micron. In this study testing procedures for prepared dental filling were according to the American dental association specification (ADA) No., 8(13) which included in the following physical properties (Table 1).

Table1: The physical properties requirements for the cement according to the ADA specification No.8

Time of setting Maximum At 37˚C (99 ˚ F) (minutes)		Minimum compressive strength (24 hours)	Maximum film thickness (mμ)		Maximum solubility and disintegration (24 hours)	Maximum arsenic content
Min.	Max.		Type I	Type II		
5	9	700 kg/cm^2 (9.956 psi)	25	40	0.2% by weight	0.0002% by weight (1:500,000)

Preparation of specimens: The preparation of all test specimens was conducted at 23 ± 2°C with 10 % relative humidity.

The powder: liquid ratio: was determined by the consistency test, mixing technique was employed in the preparation of all test specimens. The polished glass slab is approximately 150 mm long and 75 mm wide. The spatula (made of material not corroded by the cement) and the slab were clean and free from hardened particle of cement. The mixing times were 1.5 minute. The incorporation of the powder was accomplished at the rate illustrate in (table 2). At least one half of the top surface of the slab was used. No particles of powder or any unused liquid remained on the slab when the mixing completed. A linear and not a rotary motion of the spatula were used, with the edge of the spatula sweeping approximately one half of the area of the slab on each stroke. All the tests were done according to the ADA specification No 8, (Table 2).

Table 2: The incorporation of the powder liquid ratio

Proportion of total amount of powder	Time of incorporation in seconds
1/16	10
1/16	10
1/8	10
¼	15
¼	15
¼	30
	--
	90

Testing consistency. The consistency was done according to the method in the ADA specification No.8.

Time of setting. When mixing common cement, two important bearing on the acceptability of materials must be kept in mind. The first is the working time (14), defined as the time available for mixing and manipulating a material. The other time that characterizes setting is the setting time. This, like working time, is to some extent arbitrary since it is defined as the time taken for a material to have reached a certain level of rigidity or elasticity. It is known that many materials continue setting for a considerable time after the apparent setting and optimum properties may not be achieved until several hours later (14). One convenient and commonly used method to measure the setting time is resistance to penetration. Thus the material may be considered set when it is able to resist penetration by a probe of known weigh and tip diameter (14).

Compressive strength: Compressive strength is the maximal stress required fracturing a structure. It is considered to be important in restorative dental materials because compressive forces can be exerted on restorative during mastication.

Film thickness.: The thickness of the cement films is dependent on many variable among these (15,16,) :Powder-liquid ratio, the effective grain size of the cement, Geometry, Rheology, Cementation pressure and it's duration and oclusal venting of the casting. The measurement was done according the method that described in the ADA specification No.8.

Solubility and disintegration: The term, solubility and disintegration, describe the dissolution and leaching of a cement in contact with water or oral fluids (18). The solubility and disintegration of the luting cement is one of the most important properties that determine its durability in the mouth (15).

Arsenic content: The absence of arsenic were confirmed by the two methods (17).

Antimicrobial assay of the complexes

The microorganisms Staphylococcus aureus, Streptococcus mutans and Candida albicans; were selected to examine the antimicrobial activity of our complexes, all were isolated and identified at the Biology Department, College of Science, Mosul University.

We use the turbidity method (19) for the assay; 1 gm of the powdered compound was dissolved in 9 ml distilled water, then 1/10, and 1/100 concentration were prepared from the first concentration. 0.1 ml of each concentration was added to small vials contain 4 ml of the Tryptic Soya Broth medium and inoculated by 0.1 ml of the bacterial suspension, the compounds were incubated for 18 hours at 37°C. The compounds reading were at the optical density of the cultures (595 nm wavelength) by using spectrophotometer Type Spectronic 21, and the average were taken for triplicates of each compound and each concentration.

Microlekage Measurement: The extracted premolar teeth were collected and stored in tap water at room temperature. Teeth scaled and polished to remove all stains and organic debris. Teeth were examined with magnifying eye lens and teeth that showed cracks, fractures or caries lesions were excluded. A depth of (4 mm in length 2 mm in width) class (V) were performed with a tungsten carbide fissure bur on cavity (Buccal and lingual surface) for each tooth. Twenty teeth were divided into four groups of five teeth in each as follows: C= group represent the control where ZOE temporary filling (Dori-Dent). G= group Calcium oxide 70% + Guaiacol 30%. E= group Calcium oxide 70% + Eugenol 30%. M= group calcium oxide 70% + Methyl salicylate 30%.

Each cavity was filled with two increments and the excess complex was removed. All teeth were left at room temperature for two hours for complete setting time of each. Teeth were stored in 1 % Nigrosin water soluble (Fluka company) for one week. Depth of dye penetrated was assessed on optical microscope type euromex, Bi-beam and the data were collected and statistically analyzed (20). This work was conducted in the conservation department in college of Dentistry/ Mosul University.

Consistency: The average disc diameter of four mixes of different liquid: powder ratio for each cement were calculated. It was found that different consistencies of mixed cements produced discs of varying sizes and color, this relationship is clearly demonstrated, which showed 1:4(gray), 1:6(gray), 1:5(white), 1:6(gray) for C, E, G, and M respectively. As the amount of powder increased the disc diameter decreased. The amount of powder in grams which could be incorporated in 0.5 ml. of liquid to produce a consistency giving a disc of 30± 1 mm in diameter was recorded. A diameter of 29.7, 31, 30, 31 mm for cements (C), (E), (G), and (M) respectively. One way analysis of varies was performed to test the inter materials differences in consistency. It was found that there is no significant between the four brands of cements. ($F=1.229$, $p < 0.05$).

RESULTS

Setting Time: The mean setting time of the cements investigated are listed in (Table 5). The mean setting time of cement C, E, G and M were 12.12, 12.23, 7.88, 6.0 minute respectively. Statistical analysis of the data by means of analysis of variance test revealed that there is a significant different in the setting time among the four brands of cements ($F = 28.57$, $P < 0.05$). Student t-test was used to compare between brands of cements, it was concluded that there was a highly significant difference between the setting time of cement E and M ($t=7.72$, $P < 0.05$). The setting time of cement E was longer than that of cements G and this difference was statistically significant ($t=5.27$, $p < 0.05$). There was no significant difference between the setting time of cement G and M ($t = 2.45$, $p<0.05$).

Compressive strength: Mean values of compressive strength and standard deviation of the cements tested at the end 24 hours listed in (Table 5). It was found that cement E had the highest values of compressive strength among the cement tested after 24 hours whereas cement C had the lowest value, and did not meet the accepted values of the ADA specification No.8 for compressive strength. One way analysis of variance was performed to test the difference in the compressive strength of the cement tested after 24 hours. It was found that there is a highly significant difference among the four brands of cement investigated. ($t = 3.7 E + 04$, $p < 0.05$). The compressive strength of the complexes using Duncan test represented high significant between all complexes, the highest significant were E, G, M, C respectively ($p < 0.05$). Analysis of the data between different groups by t- test showed that the compressive strength of cement E was significantly higher than that of cements C ($t = 276.83$, $p< 0.05$), cement M ($t=201.69$, $p < 0.05$), and cement G ($t=157.5$, $p<0.05$).

Film thickness: The mean film thickness and standard deviation of each cement were listed in (Table 5). It was found that cement C had the lowest film thickness (30-micron) among the four tested cement and cement M had the highest film thickness (37-micron). Cements E and G had a film thickness of (35, 32 micron) respectively. ANOVA test was carried out and it was observed that there was an over-all statistical significant difference among the four brands of the cements (F=29, $p < 0.05$). Student t-test was used to compare between groups of cements. It was found a highly significant difference between the film thickness of the cement C and M cement (t=8.57, $p<0.05$). Also found highly significant difference between C cement and E cement (t=6.12, $p<0.05$). It was also found that there was a significant film thickness between cement C and G cements (t=2.45, $p<0.05$). Student test further showed that the film thickness of cement M was significantly high than of cements E (t= 2.54, $p<0.05$). G (t=6.12, $p<0.05$) and cement C (t=8.57, $p<0.05$).

Solubility and disintegration: The mean percentage and standard deviation of experiments for each cement are presented in (Table 5). Analysis of variance showed a highest significant difference between the four cements (F = 582.00, $p < 0.05$). Student t-test was used to compare between groups of cements. It was found no significant difference between the solubility of cement G and cements M (t = zero, $p < 0.05$), E (t = zero, $p < 0.05$) and C(t = zero, $p < 0.05$). It was also found that the solubility of cement G is significantly greater than that of cement C (t = 2.45, $p < 0.05$). The solubility of cements M and E are equal and both were significantly less than that of cements C and G.

Arsenic test: Arsenic test gives no color in this study which indicates a negative results.

pH measurement: The pH measurement of the prepared four cements were (7.2, 8, 10.1 and 12.2) ± 0.2 for C, G, E, and M respectively.

Microlekage test: The mean of microlekage of four cements investigated were listed in (Table 5). One way analysis of variance was performed to test the difference in the microlekage of the cement tested after 48 hours. It was found that there is a significant difference among the four brands of cements investigation (F = 14.95, $p < 0.05$).

Student t-test was performed to test inter material differences. It was found that the microlekage of cement C is significantly greater than that of cement M (t = 3.044, $p < 0.05$). The microlekage of cement E is significantly greater than that of cement M (t = 1.24, $p < 0.05$). Also it was found that the microlekage of cement C was significantly greater than that of cement G (t = 4.364, $p > 0.05$). The microlekage of cement M is significantly greater than that of cement G (t=10.402, $p< 0.05$).

Biological properties: Antimicrobial assay: The mean values of antimicrobial effect and standard deviation of the cements tested at the end of one day for *Staphylococcus aureus*, *Candida albicans* and *Streptococcus mutans* were listed in (Table 4). One way analysis of variance was performed to test the differences in their antimicrobial effects of cement tested on *Streptococcus mutans* in 1/10 and 1/100. It was found that there is a highly significant differences among the four brands of cement investigated, comparing to control (F = 13.56 and F = 652.54, $p < 0.05$) for 1/10 and 1/100 respectively. Also the test against the *Staphylococcus aureus* showed a highly significant in the two concentration (F = 64 and F = 391, $p < 0.05$) for 1/10 and 1/100 respectively.
The ANOVA analysis against *Candida albicans*, G cement had a highly significant (F = 368.66, F = 1367.43, $p < 0.05$) for 1/10 and 1/100 respectively. Duncan test was used to test inter material differences. It was found that the G cement had more antimicrobial effect against *Streptococcus mutans* in 1/10 and 1/100 concentration, *Candida albicans* 1/10 and 1/100. The M cement had a highest effect against *Staphylococcus aureus* in the two concentrations. Also E cement had highest effect against *Staphylococcus aureus* in 1/10 concentration only (F=391.34, $p<0.05$). Analysis by t-test showed the following series significant against *Streptococcus mutans*, *Candida albicans*, and *Staphylococcus aureus* (Table3).

Table 3: The effect of cement on the three different antimicrobial

Type of bacteria	1/100 concentration	1/10 concentration
Streptococcus mutans	G>M>E=C	G>M>E=C
Candida albicans	G>M>E>C	G> M>E>C
Staphylococcus aureus	M>G>C>E	E>M>C>G

G = guaiacol, M= Methyl salicylate, E= eugenol, C= control

Table 4: The effect of Streptococcus mutans, Candida albicans, Staphylococcus aureus antibacterial on cements at 1/100 and 1/10 concentration

Type of antibacterial	Type of cement									
	Control		C		M		G		E	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
Streptococcus mutans 1/100 conc.	0.5200	0.010	0.4100	0.010	0.4000	0.100	0.3900	0.010	0.4100	0.010
Streptococcus mutans 1/10conc.	0.5200	0.010	0.3600	0.01762	0.3000	0.0100	0.2103	0.010	0.3600	0.010
Candida albicans 1/100 conc	0.4190	0.0010	0.3400	0.010	0.1900	0.0100	0.1800	0.010	0. 2200	0.010
Candida albicans 1/10 conc	0.41900	0.001	0.4170	0.0100	0.0900	0.005	0.0600	0.010	0.3400	0.010
Staphylococcus aureus 1/100 conc	0.75167	0.05008	0.5000	0.1000	0.000	0.0000	0.0700	0.0100	0.6200	0.0200
Staphylococcus aureus 1/10 conc	0.5200	0.010	0.5300	0.0100	0.4400	0.0400	0.5800	0.000	0.000	0.000

Table 5: consistency, setting time, compressive strength, film thickness, solubility and disintegration of cements and microlekage for the prepared cements

Type of test	**Type of cement**							
	Control (ZOE) C		**Methylsalicylate(M**		**Guaiacol (G)**		**Eugenol (E)**	
	Mean	StDev	Mean	StDev	Mean	StDev	Mean	StDev
Consistency	29.7	± 0.816	31	± 0.957	30	± 1.00	31	± 0.816
Setting time at 37°C and 100% Humidity	±12.12	0.0908	±6.0	0.1	±7.88	0.419	±12.23	0.152
Compressive strength value after 24 hours	574.08	5.02	±806.75	5.38	±1273.75	2.5	±1533.75	4.79
film thickness	30.0	1.0	37.0	1.0	32.0	1.0	35.0	1.0
solubility and disintegration of cements	0.16	0.01	0.00	0.00	0.18	0.01	0.00	0.00
Microlekage	2.35	0.84	1.47	0.74	0.71	0.78	2.09	0.94

Table 6: The ligands and metals used with their color complexes

Complex No.	Ligand	Metal salt	Color	Complex No.	Ligand	Metal salt	Color
1	o-cresol	$BaCl_2$	P.Yellow	71	Guaiacol	$BaCl_2$	P.Yellow
2		$Ca(CH_3COO)_2$	White	72		$Ca(CH_3COO)_2$	Gray
3		$ScCl_3$	White	73		$ScCl_3$	White
4		TiCl3	Yellow	74		TiCl3	Gray
5		$VOCl_3$	D.Green	75		$VOCl_3$	Black
6		$CrCl_3$	Green	76		$CrCl_3$	Green
7		$MnCl_2.4H_2O$	Brown	77		$MnCl_2.4H_2O$	Pink
7a		$Mn(CH_3COO)_2.H_2O$	Brown	77a		$Mn(CH_3COO)_2.H_2O$	Pink
8		$FeCl_3$	D.Brown	78		$FeCl_3$	D.Red
9		$CoCl_2.6H_2O$	D.Red	79		$CoCl_2.6H_2O$	Violet
9a		$Co(CH_3COO)_2$	D.Red	79a		Co(CH3COO)$_2$	Violet
10		$NiCl_2$.6H2O	D.Brown	80		$NiCl_2.6H_2O$	Green
11		$CuCl_2.2H_2O$	D.Red	81		$CuCl_2.2H_2O$	Brown
11a		$Cu(CH_3COO)_2$	D.Red	81a		$Cu(CH_3COO)_2$	Brown
12		$ZnCl_2$	Brown	82		$ZnCl_2$	White
12a		$Zn(CH_3COO)_2$	Brown	82a		$Zn(CH_3COO)_2$	White
13		$Cd(CH_3COO)_2$	P.Brown	83		$Cd(CH_3COO)_2$	White
14		$SnCl_2$	P.Yellow	84		$SnCl_2$	P.Yellow
15	m-cresol	$BaCl_2$	P.Yellow	85	Salicylic acid	$BaCl_2$	White
16		$Ca(CH_3COO)_2$	---------	86		$Ca(CH_3COO)_2$	White
17		$ScCl_3$	White	87		$ScCl_3$	White
18		TiCl3	P.Yellow	88		TiCl3	Yellow
19		$VOCl_3$	D.Green	89		$VOCl_3$	D.Green
20		$CrCl_3$	Green	90		$CrCl_3$	Gray
21		$MnCl_2.4H_2O$	Brown	91		$MnCl_2.4H_2O$	Green
21a		$Mn(CH_3COO)_2.H_2O$	Brown	91a		$Mn(CH_3COO)_2.H_2O$	Green
22		$FeCl_3$	D.Red	92		$FeCl_3$	D.Red
23		$CoCl_2.6H_2O$	Blue	93		$CoCl_2.6H_2O$	Violet
23a		Co(CH3COO)2	Blue	93a		Co(CH3COO)2	P.Violet
24		$NiCl_2$.6H2O	Green	94		$NiCl_2$.6H2O	P.Green
25		$CuCl_2.2H_2O$	Green	95		$CuCl_2.2H_2O$	P.Green
25a		$Cu(CH_3COO)_2$	Green	95a		$Cu(CH_3COO)_2$	P.Green
26		$ZnCl_2$	White	96		$ZnCl_2$	White
26a		$Zn(CH_3COO)_2$	White	96a		$Zn(CH_3COO)_2$	White
27		$Cd(CH_3COO)_2$	Yellow	97		$Cd(CH_3COO)_2$	White
28		$SnCl_2$	Yellow	98		$SnCl_2$	P.Yellow
29	p-cresol	$BaCl_2$	Yellow	99	Thymol	$BaCl_2$	Yellow
30		$Ca(CH_3COO)_2$	--------	100		$Ca(CH_3COO)_2$	White
31		$ScCl_3$	White	101		$ScCl_3$	White
32		$TiCl_3$	Yellow	102		$TiCl_3$	White
33		$VOCl_3$	D.Green	103		$VOCl_3$	P.Blue
34		$CrCl_3$	Green	104		$CrCl_3$	Gray
35		$MnCl_2.4H_2O$	D.Red	105		$MnCl_2.4H_2O$	Brown
35a		$Mn(CH_3COO)_2.H_2O$	Red	105a		$Mn(CH_3COO)_2.H_2O$	Brown
36		$FeCl_3$	D.Red	106		$FeCl_3$	D.Red

37		$CoCl_2.6H_2O$	Green	107		$CoCl_2.6H_2O$	Green
37a		$Co(CH_3COO)_2$	Green	107a		$Co(CH_3COO)_2$	Green
38		$NiCl_2.6H2O$	P.Yellow	108		$NiCl_2.6H2O$	P.Green
39		$CuCl_2.2H_2O$	Brown	109		$CuCl_2.2H_2O$	D.Brown
39a		$Cu(CH_3COO)_2$	Brown	109a		$Cu(CH_3COO)_2$	D.Brown
40		$ZnCl_2$	P.Yellow	110		$ZnCl_2$	Brown
40a		$Zn(CH_3COO)_2$	Yellow	110a		$Zn(CH_3COO)_2$	P.Brown
41		$Cd(CH_3COO)_2$	Yellow	111		$Cd(CH_3COO)_2$	P.Yellow
42		$SnCl_2$	D.Brown	112		$SnCl_2$	Yellow
43	Eugenol	$BaCl_2$	White	113	Vanillin	$BaCl_2$	P.Yellow
44		$Ca(CH_3COO)_2$	P.Yellow	114		$Ca(CH_3COO)_2$	White
45		$ScCl_3$	White	115		$ScCl_3$	White
46		$TiCl_3$	P.Yellow	116		$TiCl_3$	White
47		$VOCl_3$	D.Green	117		$VOCl_3$	D.Red
48		$CrCl_3$	Black	118		$CrCl_3$	Green
49		$MnCl_2.4H_2O$	D.Brown	119		$MnCl_2.4H_2O$	P.Yellow
49a		$Mn(CH_3COO)_2.H_2O$	Brown	119a		$Mn(CH_3COO)_2.H_2O$	Yellow
50		$FeCl_3$	D.Red	120		$FeCl_3$	D.Red
51		$CoCl_2.6H_2O$	P.Brown	121		$CoCl_2.6H_2O$	White
51a		$Co(CH_3COO)_2$	P.Yellow	121a		$Co(CH_3COO)_2$	Gray
52		$NiCl_2.6H_2O$	Green	122		$NiCl_2.6H_2O$	Green
53		$CuCl_2.2H_2O$	Green	123		$CuCl_2.2H_2O$	Yellow
53a		$Cu(CH_3COO)_2$	Green	123a		$Cu(CH_3COO)_2$	Yellow
54		$ZnCl_2$	P.Brown	124		$ZnCl_2$	White
45a		$Zn(CH_3COO)_2$	P.Brown	124a		$Zn(CH_3COO)_2$	White
55		$Cd(CH_3COO)_2$	White	125		$Cd(CH_3COO)_2$	White
56		$SnCl_2$	P.Yellow	126		$SnCl_2$	P.Yellow
57	Methyl salicylate	$BaCl_2$	White	127	Menthol	$BaCl_2$	White
58		$Ca(CH_3COO)_2$	White	128		$Ca(CH_3COO)_2$	--------
59		$ScCl_3$	White	129		$ScCl_3$	White
60		$TiCl_3$	White	130		$TiCl_3$	Red
61		$VOCl_3$	Green	131		$VOCl_3$	D.Red
62		$CrCl_3$	Gray	132		$CrCl_3$	Blue
63		$MnCl_2.4H_2O$	Green	133		$MnCl_2.4H_2O$	Brown
63a		$Mn(CH_3COO)_2.H_2O$	Green	133a		$Mn(CH_3COO)_2.H_2O$	Brown
64		$FeCl_3$	Red	134		$FeCl_3$	Red
65		$CoCl_2.6H_2O$	Red	135		$CoCl_2.6H_2O$	Red
65a		$Co(CH_3COO)_2$	Red	135a		$Co(CH_3COO)_2$	Red
66		$NiCl_2.6H2O$	Green	136		$NiCl_2.6H2O$	Green
67		$CuCl_2.2H_2O$	Green	137		$CuCl_2.2H_2O$	Green
67a		$Cu(CH_3COO)_2$	Green	137a		$Cu(CH_3COO)_2$	Green
68		$ZnCl_2$	White	138		$ZnCl_2$	White
68a		$Zn(CH_3COO)_2$	White	138a		$Zn(CH_3COO)_2$	White
69		$Cd(CH_3COO)_2$	White	139		$Cd(CH_3COO)_2$	White
70		$SnCl_2$	P.Yellow	140		$SnCl_2$	P.Yellow

DISCUSSION

Calcium Oxide (CaO) was select as the powder to be mixed with different ligands in the study. Due to the fact it is cheap, nontoxic, neutral, white in color, available commercially, easily to be prepared. Calcium is the main consist mainly of hydroxyapatite crystals in the form of $Ca_{10}(PO_4)_6(OH)_2$ (21) .

Consistency: All the groups of cement were within the ADA specification No.8. The influence of the mixing powder: liquid ratio on dental cement properties has long been known. Paffenbarger et el.(22), Jorgensen et. al.(23), Anderson et al(24) and Wilson et al25) found that the effect can be critical, the less the amount of powder to a given quantity of liquid, the more the advance effect. Thus, in any series of comparative physical tests, a known definite of powder to liquid must to be employed and its value is established before the tests can be undertaken. The consistency of four groups of preparation cement (C, E, G, M) were within the standard consist described in ADA specification No 8 (13). All the cements were conveniently mixed, so that the results would be of comparable value. It was observed that cement M and E needed a higher amount of powder than G and C to produce the standard mix although these cements have the same chemical geometry (tetrahedral), and this could be attributed to the fact that these complexes had a different composition compounds (ligands), or row materials; and that is in agreement with Crowel observations (26).

It has been found in this study that different consistencies of mixed cements produced disks of varying sizes, and this is in agreement with Paffenberger et al.(22), Myaer et al (27) and Bruce et al.(28). The diameter of the disc decreased as the powder: liquid ratio increased for the four brands of cements and that is in agreement with Paffenberger et al.(22) and Wilson et al.(29) they reported that the diameter of the cement disc decreased as the interval between the preparation and the load application and the powder: liquid ratio were increased with decreasing the temperature and humidity(29).

Setting Time: There is a highly significant difference in the setting time of four cements; this may be attributed to the difference in their chemical structure that lead to differences in the time of reaction to form complexes, and may be due to differences in liquid /powder ratio.

Compressive strength: When an object is subjected to an axial compression it is important to recognize that the failure of the body occurs as a result of the complex stress developed in the body (30). High compressive strength of dental cements has been associated with the ability to resist forces of mastication through a restoration and with the retention of the casting (31). It has been shown that the compressive strength of the cement is an important interlocking (32). ADA specification No.8. allows a minimum compressive strength of 700 kg/cm^2 (9.956 Psi)). Cement E,G. and M proved to exceed this limit.

Cement E and G found superior in its compressive strength compared to the control C and this may be attributed to the fact that cement E and G were mixed with a high powder: liquid ratio than cement C (28). Cement C failed to meet the minimum compressive strength value required by the ADA specification No.8. Although cement M had the same powder: liquid ratio with E and higher than G, but it give low value of compressive strength. It may be attributed to the fact that cement G, and E, takes longer setting time that allow greater bond interaction between powder and liquid.

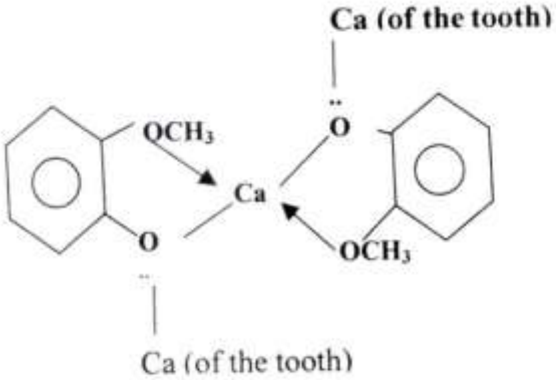
Film thickness: The film thickness values for the prepared cements meet the accepted limit (25-40 micron) in the ADA specification No.8, cement M and E showed a significantly higher film thickness than cement G and C. All of their powders had the same particle size and this may be explained that cements M and E were mixed with a higher powder: liquid ratio (16).

Solubility and disintegration: As the cement gradually dissolves, leakage occurs with subsequent loosening of the restoration and the development of secondary caries (33). The solubility of cements C, E, G and M did not exceed the maximum solubility in the ADA specification No.8.(0.2%) which makes these types of cements acceptable to be used. The solubility of cements M and E were significantly lower than that of cements G and C, this could be due to its chemical reaction which produce Calcium methyl salicylate, and calcium eugenolate complexes, it is highly insoluble complex, in addition it may be due to lower powder: liquid ratio (34).

Arsenic test: The negative results of the arsenic test indicate that the prepared cements were clear from this poisonous metal.

pH measurement: All of pH of cements with makes this type of cement within the standard of other cement. The measurement of pH for the complexes showed that the C cement was neutral while E and M are medium alkaline, cement G is slightly alkaline. Cement C represent neutral pH. This makes cement C the most convenient among them, Although other cements represented higher alkaline pH, which gave bitterness, taste and it may have an irritant effect on dental tissue, cement M may produce an irritant effect on dental tissue due to it is highly alkaline pH. The higher alkaline pH may be lowered when the cement get contact the saliva that have slightly acidic pH. In this situation there will be an acid base reaction that neutralize the high alkaline pH of the cement.

Microlekage test: Cement G found to be superior in showing no microlekage compared to that of control C, this is possibly due to the chelation between the pair of electron on the oxygen ion of complex and the calcium of tooth. It is well known that the oxygen ion (especially in phenoxides), when the conditions are suitable, can easily become tri-coordinated by binding itself to two similar (or different) metal ions using the available lone pair of electrons to form coordination bonds. Although the three cements had the same oxygen in their complexes, but in contrast to other cements, guaiacol (G) have no substitution on the ring, therefore it has no steric or inductive effect. Cements E and C posses significantly higher microlekage than that of cement M, this could be due to the fact that both cements have the same structure of ligand (eugenol) with an allyl group in the para substitution to the hydroxy group in the ring. The allyl group had a drawl effect and offer stability to the ring after chelation with a metal. The stability of the ring made it harder for bimetallic chelation to occur.



Biological properties, Antimicrobial assay: Cement G found to be superior in its antimicrobial effect against ***Streptococcus mutans*** and ***Candida albicans*** than that of the control at the two concentration (1/10 and 1/100). This may be attributed to its chemical structure. The decreases in concentration in G cement from 1/10 to 1/100 do not affect its antimicrobial activity, whereas cement E and M were represent clear antimicrobial activities against ***Streptococcus mutans*** and ***Candida albicans*** in two dilution. Cement E had high effect on a ***Staphylococcus aureus*** at 1/10 and decreases when diluted to 1/100 concentration. Cement G activity on ***Staphylococcus aureus*** increased when it is diluted to 1/100, this may be explained by the fact the more diluted solution of cement G represented better diffusion to reach the relatively thick ***Staphylococcus aureus*** membrane (35).

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