

Synthesis, Characterization and Magnetic Studies of Cobalt (II), Manganese (II) and Copper (II) Complexes containing Nitrogen-Oxygen Donor Ligands

ASMAT ZAHRA¹, TARIQ MAHMUD¹, HAZOOR AHMAD SHAD^{2*}, MUHAMMAD NAWAZ TAHIR³, HAJIRA REHMAN⁴, TANZEELA GULAB SHAHZADY⁴, ZUFIQAR ALI⁴

¹Institute of Chemistry, University of Punjab Lahore, Pakistan

²Department of Chemistry, Government Post Graduate College Jhang, Pakistan

³Department of Physics, University of Sargodha, Sargodha Pakistan

⁴Department of Chemistry, Lahore Garrison University Lahore, Pakistan

Transition metal complexes, $[M(\text{COOPh})_2(\text{TMEDA})\mu(\text{OH}_2)]$, (where $M=\text{Co}^{+2}$ and Mn^{+2}) and $[\text{Cu}_2(\text{COOPh})_2(\text{TEA})_2(\text{CH}_3\text{COO})_2]$ have been synthesized by using sodium benzoate, tetramethylethylenediamine and triethanolamine. The bonding nature and structure of complexes (1), (2) and (3) were explored through X-ray crystallography, IR, elemental analysis and magnetic studies. Single crystal X-ray analysis showed that in (1) and (2) complexes, each M (II) is bridged by two benzoate ions, one TMEDA and one water molecule while in (3) complex, Cu1 is coordinated by four oxygen atoms, two from TEA and two from carboxylate group while Cu2 is coordinated by three oxygen atoms and one nitrogen atom. All three complexes displayed triclinic system with space group P-1. Vibrating sample magnetometer measurement justified that these complexes are soft magnetic materials and can retain a certain value of magnetization even when magnetic field is removed.

Keywords: Tetramethylethylenediamine; Triethanolamine; Binuclear complex; Soft magnetic material; Metallo-enzymes.

Transition metal carboxylate clusters have attracted much attention because these clusters are a part of active sites of metallo-enzymes [1] and also show novel magnetic properties [2]. Tetranuclear Mn is the commonly known oligo nuclear cluster present in active site of photo system II. It carries oxidation of water to molecular di-oxygen [3–7]. In biology metallo-proteins having Mn^{+2} and Co^{+2} sites play an important role [8]. In addition to B12, cobalt proteins are also known. These proteins comprise methionine amino peptidase 2. This enzyme occurs in human and other mammals not having B12 corrin ring. Nitriles hydratase is another non corrin cobalt enzyme that metabolizes nitrile in bacteria [9]. Other enzymes are methionyl amino peptidase, methylmalonyl-CoA mutase, isobutyryl-CoA mutase [10]. Active sites of all these metallo-enzymes may have mononuclear or dinuclear metal complexes [11, 12]. In all these compounds ligation of metal ion is provided by O and N donor atoms from various amino groups of metallo proteins. Enzymes having Mn as co-factor are also known including: transferases, hydrolases, oxidoreductases, isomerases, lyases, ligases, lectins, and integrins. Pseudocatalases from *Lactobacillus plantarum* [13] and *Thermus thermophiles* and certain ribonucleotides reductases (RNR), also have binuclear Mn sites these enzymes catalyze the disproportionation of H_2O_2 and reduction of ribonucleotides respectively. Arginase is polypeptides having manganese metals [14].

Most commonly used metals Fe (II) Co (II) Ni (II), Zn (II) Mn(II) form low molecular weight complexes that have importance for molecular based magnets [15]. These complexes possessed high catalyst activity; therefore, these are extremely important for biological chemists [16–21]. Many dicarboxylic and diamines based Cu (II) complexes have already been reported [22–26]. Such

complexes have significance for the synthesis of copper containing superconducting ceramics [27]. Copper is an important trace metal for plants and animals [28,29] and its mixed ligand complex are involved in a number of biological processes [30–32]. Cu(II) complexes are used in treatment of many diseases including cancer [33,34]. Numerous complexes having dinuclear μ -Oxo or μ -hydroxo bridged by μ -O-O carboxylate ligands have already been reported. Binuclear, trinuclear and tetranuclear complexes having O- and N- containing donor atoms have been synthesized [35–47]. Keeping in view importance of these metal complexes, here we are reporting Co^{+2} , Mn^{+2} and Cu^{+2} complexes having μ bridging by O- and N- atoms. Molecular structures of compounds (1), (2) and (3) have been determined by X-ray crystallographic method. Tetramethylethylenediamine and triethanolamine are bidentate ligands and form five membered chelate rings, while benzoic acid is bidentate ligand and forms binuclear Co (II), Mn (II) and trinuclear complexes. These ligands show variable coordination modes with various metal ions because of presence of -COOH and -NH₂ groups.

Experimental part

Physical Measurements

All starting chemicals were of analytical grades used without further purification. Metal ions were used as their acetate salts. C, H, N elemental analyses were carried out by Perkin Elmer USA model analyzer. Infrared spectra were recorded (400–4000 cm^{-1}) on SHIMADZU FT-IR spectrophotometer. Magnetic measurements were done by using Vibrating Sample Magnetometer (Lakeshore's 7407) at 298 K by applying field strength of 0–10000. Crystal study of both complexes was done by single crystal X-ray

* email: hazoorahmad@gmail.com

diffraction technique by using APEX2 BRUKER diffractometer using SAINT program to solve structures.

Synthesis of Complexes (1), (2) and (3)

Methanol (10 mL) solution of tetramethylethylenediamine 0.116 g (1.0 mmol) was mixed with aqueous (10 mL) solutions of tetra hydrated cobalt acetate 0.249 g (1.0 mmol). The mixture was stirred for 15 min. Meanwhile, methanol (10 mL) solution of sodium benzoate 0.144 (1.0 mmol) was added drop wise and the mixture was further stirred for 1h at room temperature. The reaction was monitored through TLC. After the completion of reaction, mixture was filtered. The filtrate was left for slow evaporation at room temperature. After a week, pink prisms of suitable size for crystallography were obtained. Crystals were collected and washed with methanol, dried in air and used for characterization. Crystals were found stable under air, light and exposure to x-rays. Same method was applied to prepare manganese (II) complex (2). On the other hand, for the synthesis of Cu (II) complex, methanol (10 mL) solution of triethanolamine 0.186g (1.25 mmol) was used instead of TMEDA rest of the procedure was same as for complex (1) and (2).

Results and discussions

Chemistry

Complexes (1) and (2) were prepared by the reaction of equimolar quantity of tetramethylethylenediamine, cobalt acetate and sodium benzoate in methanol. While the complex (3), was synthesized by the reaction of methanolic solution of copper acetate and triethanolamine with sodium benzoate. The desired complexes were obtained successfully in good yield (78–85%). The products were obtained as crystalline solids and their purities were checked by thin layer chromatography. The complexes were soluble in various solvents such as ethanol, methanol, 1, 4-dioxane, DMF and DMSO. The composition of the complexes was consistent with their microanalytical data as reported in tables 6 and 7. The metal ions in complex

(1) and (2) are hexa-coordinated with four O-atoms and two N-atoms. In these complex, four oxygen atoms comes from two bridging benzoate ligands and two monodentate benzoate ligands, while two N-atoms come from a chelated tetra-methylethylenediamine. The coordination around each metal is completed by a water molecule making a μ -bridging. In complex (3), two copper atoms are coordinated with four ligands. Cu1 is coordinated by four oxygen atoms while Cu2 is coordinated by three oxygen atom and one nitrogen atoms.

X-ray Crystal Structure

The molecular structure of $[M(\text{COOPh})_2(\text{TMEDA})_\mu(\text{OH})_2]$ (where $M = \text{Co}^{+2}$ and Mn^{+2}) and $[\text{Cu}_2(\text{COOPh})_2(\text{TEA})_2(\text{CH}_3\text{COO})_2]$ with atom numbering scheme is shown in figures 1–3. The crystallographic data, selected bond lengths, bond angles and torsion angles are given in tables 1–5, respectively. Crystal structures of complexes (1) and (2) are iso-structural. The coordination around each metal ion is similar with minor variations of bond distances and bond angles.

The crystallographic data showed that the Co1–O and Co2–O bond distances are in the range [2.289(2) Å to 2.554(2) Å] and 2.289(2) Å to 2.554(2) Å], respectively. The Co1–N and Co2–N bond distances are [2.289(2) Å, 2.554(2) Å] and [2.289(2) Å, 2.554(2) Å], respectively. Co1–N bond distance is 2.642(2) Å. The Mn1–O and Mn2–O bond distances are in the range [2.109(2) Å to 2.209(2) Å] and [2.102(2) to 2.214(2) Å], respectively. The Mn1–N and Mn2–N bond distances are [2.334(3) Å, 2.363(3) Å] and [2.321(3) Å, 2.371(3) Å], respectively. The Co1...Co2 and Mn1...Mn2 separations are 3.5870(5) Å and 3.6100(7) Å respectively as shown in table 2. The coordination sphere of Co (II) and Mn (II)-ions is six, four O-atoms and two N-atoms (ORTEP figs. 1 and 3 respectively). The basal planes of distorted octahedrons consist of three O-atoms and an N-atom (O-atom of bridging water, its opposite N-atom, O-atom of mono-dentate benzoate and its opposite O-atom of bridging benzoate). The other N-atom and O-atom

Crystal Data	Complex (1)	Complex (2)	Complex (3)
Chemical formula	C ₄₀ H ₅₄ Co ₂ N ₄ O ₉	C ₄₀ H ₅₄ Mn ₂ N ₄ O ₉	C ₃₀ H ₄₄ Cu ₂ N ₂ O ₁₄
Mr	852.73	844.75	847.29
Crystal size (mm)	0.35 × 0.30 × 0.20	0.35 × 0.24 × 0.18	0.32 × 0.260 × 0.240
Shape	Prism	Prism	Prism
Color	Pink	Yellow	Blue
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1
T (K)	296	296	296
a (Å)	10.8327 (4)	10.9179 (6)	7.7322(8)
b (Å)	11.8285 (4)	11.9234 (7)	10.5913(11)
c (Å)	17.2167 (6)	17.3794 (10)	11.0476(11)
α (°)	105.558 (2)	105.682 (3)	104.723(4)
β (°)	91.731 (2)	92.353 (3)	90.006(4)
γ (°)	92.877 (2)	92.343 (3)	96.616(4)
V (Å ³)	2120.36 (13)	2173.2 (2)	868.79(15)
Z	2	2	1
R _{int}	0.049	0.071	0.064
Data with I > 2 σ (I)	34097, 9633, 6174	34915, 10004, 4999	
No. of Parameters	512	510	226
No of reflections	9633	10004	12857
R, wR(F ²), (sin θ/λ) _{max} (Å ⁻¹)	0.044, 0.119, 1.02	0.057, 0.142, 1.00	0.046, 0.089, 0.935
wR2 (all data)	0.650	0.652	0.1073
Largest residuals(e.Å ⁻³)	0.40, -0.45	0.38, -0.31	0.424, -0.543

Table 1
CRYSTALLOGRAPHIC
DATA FOR COMPLEXES
(1), (2) AND (3)

Bond Length	Complex (1)	Complex (2)	Complex (3)
M1—O3	2.0487 (17)	2.108 (2)	Cu1—O3 1.902 (3)
M1—O5	2.0719 (19)	2.147 (2)	Cu1—O1 1.963 (3)
M1—O9	2.1264 (18)	2.206 (2)	Cu2—O3 1.922 (2)
M1—O1	2.1294 (19)	2.208 (2)	Cu2—O6 1.948 (3)
M1—N1	2.220 (2)	2.334 (3)	Cu2—O2 1.965 (3)
M1—N2	2.246 (2)	2.364 (3)	Cu2—N1 2.064 (3)
M2—O6	2.0396 (19)	2.100 (2)	O7—C9 1.241 (5)
M2—O4	2.0596 (17)	2.140 (2)	N1—C4 1.504 (5)
M2—O7	2.0953 (16)	2.163 (2)	O6—C9 1.281 (5)
M2—O9	2.1304 (17)	2.214 (2)	O1—C1 1.250 (4)
M2—N3	2.213 (2)	2.319 (3)	O2—C1 1.256 (5)
M2—N4	2.251 (2)	2.370 (3)	O3—C3 1.426 (5)
O9—H9A	0.84 (3) 0.93 (3)	N1—C5 1.494 (5)	
O9—H9B	0.96 (4) 0.94 (4)	N1—C7 1.487 (5)	
			O4—C6 1.418 (5)
			O5—C8 1.425 (5)

Table 2
IMPORTANT BOND LENGTHS (Å)
OF COMPLEXES (1) AND (2)

Selected parameter	Angle (°)	Selected parameter	Angle (°)
O3 ⁱ —Cu1—O3	180	C9—O6—Cu2	131.8 (3)
O3 ⁱ —Cu1—O1	91.57 (11)	C7—N1—C5	109.0 (3)
O3—Cu1—O1	88.43 (11)	C7—N1—C4	111.1 (3)
O3 ⁱ —Cu1—O1 ⁱ	88.43 (11)	C5—N1—C4	111.3 (3)
O3—Cu1—O1 ⁱ	91.57 (11)	C7—N1—Cu2	108.4 (2)
O1—Cu1—O1 ⁱ	180.00 (14)	C5—N1—Cu2	110.1 (2)
O3—Cu2—O6	175.31 (12)	C4—N1—Cu2	107.0 (2)
O3—Cu2—O2	92.68 (11)	O1—C1—O2	125.9 (4)
O6—Cu2—O2	87.79 (11)	O1—C1—C2	116.1 (4)
O3—Cu2—N1	85.96 (11)	O2—C1—C2	118.0 (4)
O6—Cu2—N1	93.58 (12)	O3—C3—C4	109.8 (3)
O2—Cu2—N1	178.63 (12)	N1—C4—C3	109.8 (3)
C1—O1—Cu1	134.6 (3)	N1—C5—C6	112.5 (3)
C1—O2—Cu2	126.0 (2)	O4—C6—C5	109.7 (4)
C3—O3—Cu1	124.8 (2)	N1—C7—C8	114.4 (3)
C3—O3—Cu2	108.9 (2)	O5—C8—C7	113.8 (3)

Table 3
IMPORTANT BOND ANGLES (°) OF
COMPLEX (3)

Selected parameter	Angle (°)	Selected parameter	Angle (°)
C2—C1—N1—Co1	-21.6 (6)	C2—C1—N1—Mn1	-5.1 (9)
C1—C2—N2—C6	93.3 (6)	C1—C2—N2—C6	110.7 (9)
C1—C2—N2—C5	-149.1 (5)	C1—C2—N2—C5	-131.8 (9)
C1—C2—N2—Co1	-30.2 (6)	C1—C2—N2—Mn1	-12.1 (10)
C36—C35—N3—C37	81.0 (3)	C36—C35—N3—C37	84.2 (4)
C36—C35—N3—C38	-160.6 (3)	C36—C35—N3—C38	-157.2 (4)
C36—C35—N3—Co2	-40.7 (3)	C36—C35—N3—Mn2	-38.2 (4)
C35—C36—N4—C40	78.9 (4)	C35—C36—N4—C40	82.1 (5)
C35—C36—N4—C39	-163.7 (3)	C35—C36—N4—C39	-160.2 (4)
C35—C36—N4—Co2	-43.4 (3)	C35—C36—N4—Mn2	-40.4 (5)
O2—C7—O1—Co1	4.2 (4)	O2—C7—O1—Mn1	4.8 (5)
C8—C7—O1—Co1	-177.94 (15)	C8—C7—O1—Mn1	-176.39 (15)
O4—C14—O3—Co1	-12.1 (5)	O4—C14—O3—Mn1	-11.2 (6)
C15—C14—O3—Co1	168.39 (19)	C15—C14—O3—Mn1	168.9 (2)
O3—C14—O4—Co2	9.4 (5)	O3—C14—O4—Mn2	3.2 (5)
C15—C14—O4—Co2	-171.08 (17)	C15—C14—O4—Mn2	-176.9 (2)
O6—C21—O5—Co1	-2.0 (4)	O6—C21—O5—Mn1	-2.5 (5)
C22—C21—O5—Co1	179.08 (16)	C22—C21—O5—Mn1	177.3 (2)
O5—C21—O6—Co2	-8.4 (4)	O5—C21—O6—Mn2	-16.2 (5)
C22—C21—O6—Co2	170.60 (18)	C22—C21—O6—Mn2	164.0 (2)
O8—C28—O7—Co2	7.0 (4)	O8—C28—O7—Mn2	3.7 (5)
C29—C28—O7—Co2	-174.38 (16)	C29—C28—O7—Mn2	-177.8 (2)

Table 4
SELECTED TORSION
ANGLES (°) OF
COMPLEXES (1)
AND (2)

are at apical positions. In each bi-nuclear complex one of the tetramethylethylenediamine and mono-dentate benzoate (attached to same metal ion) are disordered due to ethyl and benzene ring with occupancy ratio of

0.662(5):0.338(5). The role of water molecule is to provide bridging between metal ions through O-atom and to stabilize the orientation of mono-dentate benzoate groups due to H-bonding.

Selected parameter	Angle (°)	Selected parameter	Angle (°)
Cu1—O1—C1—O2	13.4 (7)	Cu2—N1—C7—C8	-49.2 (4)
Cu1—O1—C1—C2	-167.6 (3)	N1—C7—C8—O5	53.5 (5)
Cu2—O2—C1—O1	-9.8 (7)	Cu2—O6—C9—O7	11.3 (6)
Cu2—O2—C1—C2	171.2 (3)	Cu2—O6—C9—C10	-165.9 (2)
Cu1—O3—C3—C4	88.5 (3)	O7—C9—C10—C11	-175.9 (4)
Cu2—O3—C3—C4	-46.2 (3)	O6—C9—C10—C11	1.4 (5)
C7—N1—C4—C3	-137.6 (4)	O7—C9—C10—C15	0.7 (6)
C5—N1—C4—C3	100.8 (4)	O6—C9—C10—C15	178.0 (3)
Cu2—N1—C4—C3	-19.6 (4)	C4—N1—C7—C8	68.0 (4)
O3—C3—C4—N1	43.4 (4)	C5—N1—C7—C8	-169.1 (3)
C7—N1—C5—C6	175.8 (3)	N1—C5—C6—O4	-49.6 (5)
C4—N1—C5—C6	-61.4 (4)	Cu2—N1—C5—C6	57.0 (4)

Table 5
SELECTED TORSION
ANGLES (°) OF
COMPLEX (3)

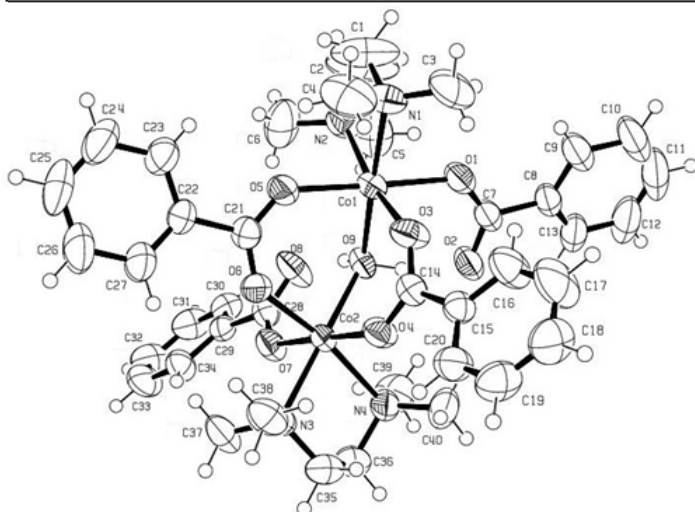


Fig. 1. ORTEP Diagram of Complex (1)

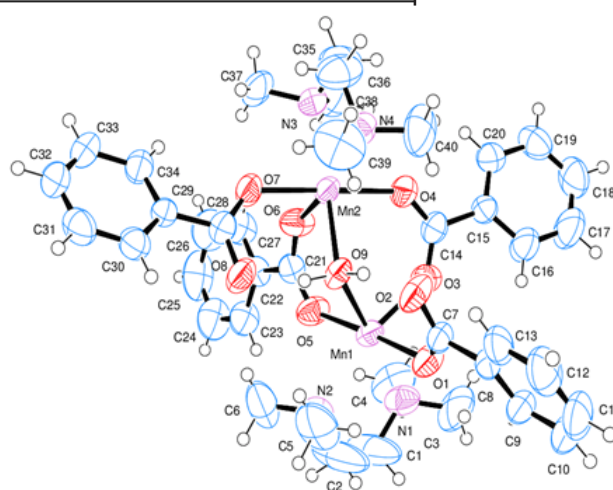


Fig. 2. ORTEP Diagram of Complex (2)

In both complexes none of the benzoate ligand is planar. For example, the dihedral angle between the carboxylate group *A* (O1/C7/O2) and benzene rings *B* (C8a–C13a) is 12.5(6)°. The minor part of disordered benzene ring *C* (C8b–C13b) is oriented at a dihedral angle of 2.6(7)° with its major counterpart *B*. For other benzoates the dihedral angle between *D*(O3/C14/O3)/*E*(C15–C20), *F*(O5/C21/O6)/*G*(C22–C27) and *H*(O7/C28/O8)/*I*(C29–C34) is 20.5(2)°, 9.9(5)° and 18.9(3)°, respectively. The dihedral angles between *B/E*, *E/G* and *G/I* is 86.8 (2)°, 64.99(11)° and 84.8(1)° respectively.

Crystallographic data of complex (3) shows that the bond distances between Cu1–O1, Cu1–O1i and Cu–O3i are in the range of 1.963(32), 1.963(3) and 1.902(3), respectively. Similarly, the bond distances between Cu2–O3, Cu2–O6 and Cu2–O2 are 1.922(2), 1.948(3) and 1.965(3) respectively as shown in table 2. Bond distance of Cu1–O3 from triethanolamine is 1.902(3) while Cu2–N1 from triethanolamine is 2.064(3). The geometry around the Cu atom is square planar due to three oxygen atoms and one nitrogen atom. It is coordinated with one oxygen atom from carboxylate ion (Cu2–O6), second from acetate ion (Cu2–O2) and third from triethanolamine (Cu2–O3). The angles around the copper atom, O6/Cu2/N1, N1/Cu2/O3, O3/Cu2/O2 and O2/Cu2/O6 are 93.58 (12), 85.96 (11), 92.68 (11) and 87.79 (11) respectively which are deviated from normal angle (90°) to some extent due to presence of different groups attached at four corners of square planar geometry. In the same way, Cu1 is also coordinated by four oxygen atoms i.e. two from acetate groups (Cu1–O1 and Cu1–O1i) while other two from triethanolamine (Cu1–O3 and Cu1–O3i).

Benzoate ligand in copper complex is non-planar from the basal plane. The dihedral angle between carboxylate

group *A*(C9/O6/Cu2) and benzene ring *B*(C10–C15) is 17.625°.

Infrared Spectroscopy

Several characteristics bands have been observed in IR spectrum of complexes (1), (2) and (3). Sodium benzoate, TMEDA and TEA ligand have a tendency to coordinate with metal due to donor atoms. Co and Mn Complexes showed bands at 3387 and 3352 respectively which are assigned to –OH group indicates the presence of H₂O molecule in both the complexes. Bands observed at 1541, 1544, 1540 and at 1394, 1400, 1402 are assigned to C=O and C–O in Co, Mn and Cu complexes respectively that indicates the presence of carboxylic group in these complexes. In addition to these two new bands appeared due to the presence of M–N and M–O in these complexes (table 6). Appearance of these peaks indicates the coordination of Co, Mn and Cu with ligands.

Elemental Analyses

The observed and experimental values of CHN analysis are given in table 7. These elemental analyses showed that % of C, % H and % N are almost same in all three complexes with small variation up to 5%.

Magnetic Measurements

Vibrating sample magnetometer (VSM) was used to carry out magnetic measurement. Magnetic behavior of complexes (1), (2) and (3) are shown in figures 4, 5 and 6 respectively. The plot between magnetic field (G) and magnetic moment (emu) indicates that these complexes are ferromagnetic in nature and magnetism is reversible. These materials are magnetically anisotropic. Low value of coercivity and retentivity indicate that all three

Group	Complex (1)	Complex (2)	Complex (3)
OH	3387	3352	-
C=O	1541	1544	1540
C-O	1394	1400	1402
M-N	453	449	450
M-O	565	559	560

Table 6
IMPORTANT IR PEAKS (CM⁻¹) OBSERVED FOR COMPLEXES (1), (2) AND (3)

Elemental analysis	%C	%H	%N
For complex (1)	57.56 (57.42)	6.51(6.58)	5.53(5.56)
For complex (2)	57.75(57.68)	6.72(6.64)	5.22(5.18)
For complex (3)	47.11(47.68)	7.51(7.57)	6.54(6.10)

Table 7
ELEMENTAL ANALYSES FOR COMPLEXES (1), (2) AND (3)

%age of elements shown in parenthesis () are calculated values.

VSM Analysis	Coercivity (Hci) G	Magnetization (Ms) emu	Retentivity (Mr) emu	Squareness ratio
Complex (1)	223.57	2.5625×10^{-3}	127.43×10^{-6}	49.728×10^{-3}
Complex (2)	235.94	2.2829×10^{-3}	105.10×10^{-6}	46.037×10^{-3}
Complex (3)	245.81	2.1729×10^{-3}	101.50×10^{-6}	46.117×10^{-3}

Table 8
VSM CALCULATION FOR COMPLEXES (1), (2) AND (3)

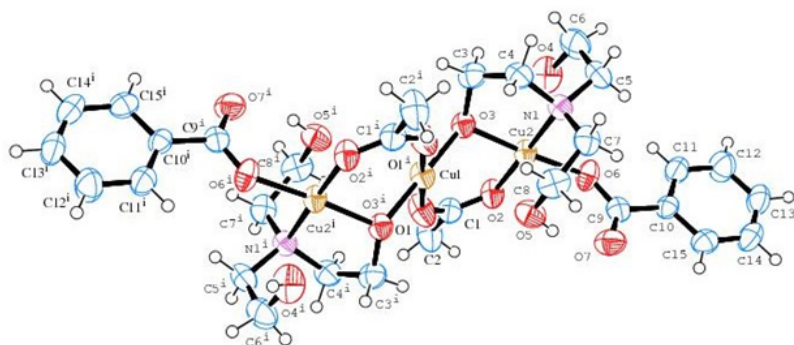


Fig. 3. ORTEP Diagram of Complex (3)

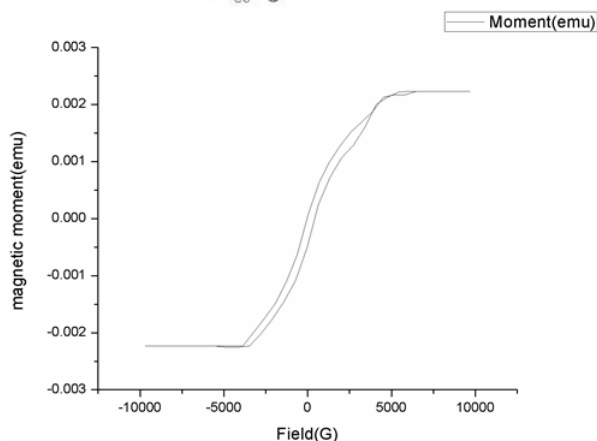


Fig. 4. Hysteresis Loop for Complex (1)

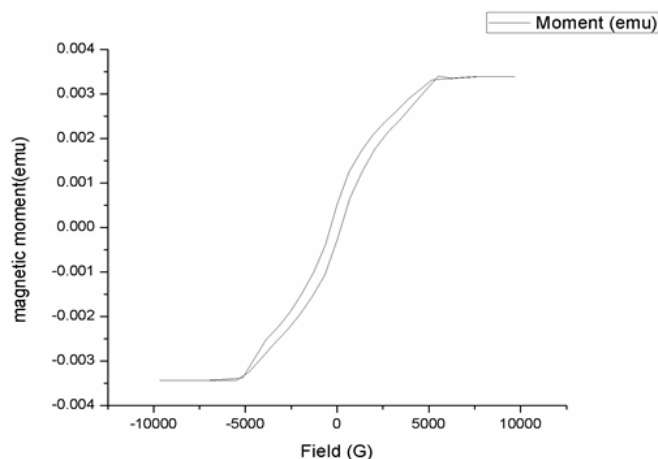


Fig. 6. Hysteresis Loop for Complex (3)

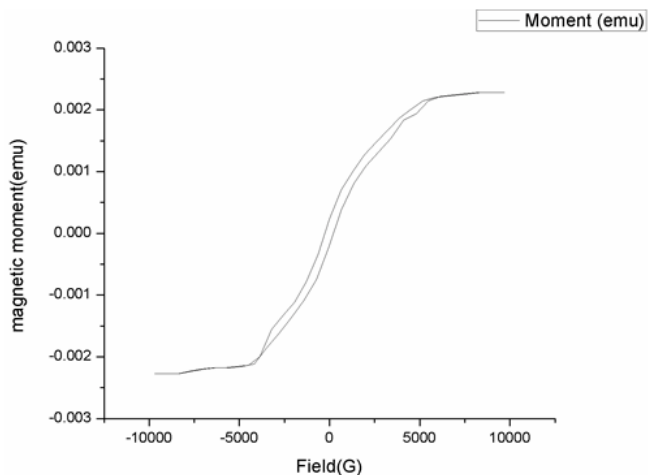


Fig. 5. Hysteresis Loop for Complex (2)

complexes are soft magnetic materials. Coercivity of a magnetic material is related with its microstructure. At 9685.95 G field complex (1) showed a magnetic moment of 2.232×10^{-3} emu, complex (2) showed a magnetic moment of 2.235 emu while complex (3) showed a magnetic moment of 2.345×10^{-3} emu. Value of saturation of magnetization and squareness ratio obtained from VSM analysis are presented in table 8.

Conclusions

Three complexes of Co (II), Mn (II) and Cu (II) were synthesized. Magnetic studies of complexes proved that all three complexes are soft magnetic materials. These complexes showed certain values of magnetization saturation that is property of ferromagnetic and antiferromagnetic materials. These materials can show a

certain value magnetic moment even in the absence of magnetic field without becoming demagnetized. It is seen that Co (II) complex showed good magnetic properties than Mn (II) and Cu (II) complex.

Acknowledgement: One of us (AZ) is gratefully to Higher Education Commission (HEC), Government of Pakistan for the award of financial support to carry out this research.

References

1. PECORARO, V.L. Manganese Redox Enzymes, VCH Publishers, New York, NY, USA, 1992.
2. BAGAI, R., CHRISTOU, G. Chem.Soc.Revi. **38**(4), 2009, 1011-1026.
3. BARBER, J., Chem.Soc.Revi. **38**(1), 2009, 18-196.
4. MUKHOPADHYAY, S., MANDAL, S.K. BHADURI, S., ARMSTRONG, W.H., Chem.Soc.Revi. **104**(9), 2004, 3981-4026.
5. MISHRA, W. WERNSDORFER, K. A. ABBOUD, CHRISTOU, G., Chemi.Comm. **1**, 2005, 54-56.
6. RUTTINGER, W., DISMUKES, G.C. Chem.Soc.Revi. **97**(1), 1997, 1-24.
7. MANCHANDA, R., BRUDVIG, G.W., CRABTREE, R.H. Coord.Chem.Revi. **144**, 1995, 1- 38.
- 8.*** (a) Manganese Redox Enzyme; PECORARO, V.L., Ed. VCH: New York, 1992. (b) DISMUKES, G.C. Chem.Rev. **96**, 1996, 2909-2926.
9. KOBAYASHI, MICHIIHIKO, SHIMIZU, SAKAYO. Eur.Biochem., **261**(1), 1999, 1-9.
10. CRACAN, VALENTINE, BANERJEE, RUMA (2013). Cobalt and corrinoid transport and biochemistry. In Baanci, Lucia (Ed.). Metallomics and the cell. Metal ions in life sciences 12.
11. PECORARO, V.L., BALDWIN, M.J., GELASCO, A. Chem.Revi., **94**(3), 1994, 807-826.
12. WU, A.J., PENNER-HAHN J.E., PECORARO, V.L. Chem.Revi. **104**(2), 2004, 903-938.
13. (a) KONO, Y., FRIDOVITCH, I., J.BIOL.CHEM., 258, 1983, 6015 (b) BEYER, W.F., JR., FRIDOVITCH, I. J. BIOCHEM., 24, 1985, 6460.
14. LAW, N., CAUDLE, M., PECORARO, V. Advances in Inorganic Chem. 46, 1998, 305.
15. YAKHMI, J.V. Bull.Mater.Sci. **32**, 2009, 217-225.
16. MURPHY, B.P. Coord.Chem.Rev. **124**, 1993, 63.
17. PIERRE, J.L. CHAUTEPS, P. REFAIF, S. BEGUIN, C. MARZOUKI, A.E. SERRATRICE, G. SAINT-AMAN, E. REY, P., J.Am.Chem.Soc. **117**, 1995, 1965.
18. MAO, Z.W. CHEN, D. TANG, W.X. YU, K.B. LIU, L., Polyhedron **11**, 1992, 191.
19. PATEL, R.N., KUMAR, S., PANDEYA, K.B., Spectrochim.Acta A **56**, 2000, 2791.
20. KUMAR, S., PATEL, R.N., KHADIKAR, P.V., PANDEYA, K.B., Proc. Indian Acad. Sci. (Chem.Sci.) **113**, 2001, 21.
21. PATEL, R.N., KUMAR, S., PANDEYA, K.B., J.Inorg.Biochem. **89**, 2002, 61.
22. PATEL, R.N., Spectrochim. Acta A **59**, 2003, 713.
23. O'BRIEN, P., STAFFORD, C., YOUNG, L.C., J.Inorg.Chim.Acta **147**, 1988, 3-4.
24. O'BRIEN, P., J.Coord.Chem.Rev. **58**, 1984, 169.
25. AFZAAL, M., FLYNN, E., MALIK, M.A., O'BRIEN, P., MOTEVALLI, M., Polyhedron **24**, 2005, 1101.
26. YAO, K.L., ZHANG, J.Q., LIU, Z.L., GAO, G.Y., LI, Y.L., XI, D., NING, Q., J.Magn. Magn.Mater. **320**, 2008, 458.
27. SHEN, H.Y., BU, W.M., LIAO, D.Z., JIANG, Z.H., YAN, S.P., WANG, G.L., J.Inorg. Chem.Comm., **3**, 2000, 497.
28. YASUMICHI, M., JUKICHI, H., YOSHIKI, Y., MINORU, N., AKIRA, C., Appl.Phys.Lett. **56**, 1990, 1585-1587.
29. SORENSON, J.R.J. Chem.Br. **16**, 1984, 1110.
30. GOUCH, R.K., KENSLER, T.W., OBERLEY, L.W., SORENSON R.J., KARLIN, K.D., J. Zubieta (Eds.), Biochemical and Inorganic Copper Chemistry, Vol. 1, Adenine, New York, 1986, p. 139.
31. BACA, S.G., SEVRYUGINA, Y., CLERAC, R., MALAESTEAN, I., GERBELEU, N., PETRUKHINA, M.A., Inorg.Chem.Comm., **8**(5), 2005, 474-478.
32. MENAGE, S., VITOLS, S.E., BERGERAT.P., et al., Inorg.Chem., **30**, 1991, 2666-2671.
33. FERNANDEZ, G., CORBELLA, M., MAHIA, J., MAESTRO, M.A., Eur.Inorg.Chem., **9**, 2002, 2502-2510.
34. TSUNEOYOSHI, K., KOBAYASHI, H., MIYAMAE, H. ActaCryst.C, **49**, 1993, 233-236.
35. RARDIN, R.L., POGANIUCH, P., BINO, A., et al., J.Am.Chem.Soc., **114**(13), 1992, 5240-5249.
36. WANG, M., MA, C.B., WANG, H.S., CHEN C.N., LIU, Q.T., J.Mol.Str., **873**(1-3), 2008, 94-100.
37. TANGOULIS, V., MALAMATAR, D.A., et al., Inorg.Chem, **35**(17), 1996, 4974-4983.
38. GOMEZ, V., MALAMATAR, D.A., SOULTI, K., et al., Eur. J. Inorg. Chem., **29-30**, 2009, 4471-4482.
39. STOUPOS, C.C., GASS, I.A., MILIOS, C.J., et al., Inorg.Chem.Comm, **11**(2), 2008, 196-202.
40. MILIOS, C. J., STAMATATOS, T. C., KYRITSIS, P., et al., Eur.J. Inorg.Chem, **14**, 2004, 2885-2901.
41. KLOSKOWSKI, M., PURSCHE, D., HOFFMANN, R.D., et al., Zeitschrift fur Anorganische and Allgemeine Chemie, **633**(1), 2007, 106-112.
42. ASADA, H., HAYASHI, K., NEGORO, S., FUJIWARA, M., MATSUSHITA, T., Inorg.Chem.Comm, **6**(2), 2003, 193-196.
43. PURSCHE, D., TRILLER, M.U., REDDIG, N., ROMPEL, A., KREBS, B., Zeitschrift fur Anorganische und Allgemeine Chemie, **629**(1), 2003, 24-28.
44. KESSISSOGLOU, D.P., KIRK, M.L., LAH, M.S., et al., Inorg.Chem., **31**(26), 1992, 5424-5432.
45. BHADURI, S., PINK, M., CHRISTOU, G., Chem.Comm., **20**, 2002, 2352-2353.
46. ZARTILAS, S., MOUSHI, E.E., NASTOPOULOS, V., BOUDALIS, A.K., TASIPOULOS, A.J., Inorg.Chimi.Acta, **361**(14-15), 2008, 4100-4106.

Manuscript received: 6.06.2017