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Synthesis, Characterizations, Crystal Structure Determination of μ^6 Coordinated Complex of Co (III) with EDTA and Its Thermal Properties

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*The monomeric coordination complex (**I**) is having formula **{[Co(III)-μ^6-(H-EDTA-κ^5 N1,N2,O2,O6,O8)·H_2O]·2H_2O}**, which has been crystallized in distilled water and characterized by elemental analyses, FT-IR spectrum and Powder X-ray diffraction analyses. Single-crystal X-ray diffraction analysis revealed that complex (**I**) crystallized in triclinic space group **P-1** (space group no. 2) having μ^6 coordination modes of complex with EDTA and Co (III) transition metal ion. The coordination number of Co (III) ion is six, occupied distorted octahedral geometry, where three carboxylate oxygen atoms, two nitrogen atoms, and one water molecule O1W are coordinated. There are two lattice water molecules are present in the molecular structure of complex (**I**) responsible for strong H-bonding interactions.*

Keywords Coordination mode; octahedral geometry; space group; transition metal ion

1. Introduction

There are interesting coordination polymers reported in the literature, based on multi-functional bridging ligands due to their fascinating structures and promising applications in practical fields such as magnetism [1], and catalysis [2], medicine [3], electrochemistry [4], etc. The multidentate ligands are having various coordination sites for synthesis of coordination polymers by incorporating transition metals [5–9] and lanthanides [10], etc. There are various geometrical arrangements of multidentate ligands and variation in coordination numbers can be achieved depending upon the requirements of the cations involved. The coordination compounds with different geometries have been produced with wide range of metal salts and multidentate ligands also depending upon the environmental and reaction conditions. EDTA is demonstrated as one of the desirable ligands because of its several coordination sites and flexible connection modes such as IDA (iminodiacetic acid) [11], NTA (nitrilotriacetic acid) [12], and CDTA (1, 2-cyclohexanedinitrilo-tetraacetic acid) [13]. This ligand is having four carboxylate groups with 10 potentially coordination sites (eight O atoms and two N atoms). The deprotonated EDTA can act as a tetradenate, pentadentate or hexadentate ligand to form a six-coordinate octahedron, seven-coordinate

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distorted monocapped trigonal prism or pentagonal bipyramid, often with one or more water molecule as a sixth or seventh ligand, respectively. For example, hexadentate EDTA-Co compounds $[NH_4][CO^{III}(EDTA)]$, $[Co(H_2O)_4][CO^{II}(EDTA)]CoII(EDTA)\cdot 2H_2O]$, $CO^{II}{}_2(EDTA)\text{-}(H_2O)]$, and $[CO(H_2O)_6][Co^{II}(EDTAH)(H_2O]\cdot 2H_2O]$ occupied octahedral geometry [14–17], seven coordinate hexadentate EDTA {M = Mn, Ti, and Fe] with one coordinated water [18–20], six coordinated complex with a pentadentate EDTA with one acetate group unattached and a coordinated water molecule completing the octahedron, [M = Ni(II), Co(III), Cu(II), and Fe(III)] [21–24]. We have synthesized monomeric complex using EDTA as multidentate ligand with Co (III) metal ion, adopts distorted octahedral geometry [25] with μ^6-EDTA coordination mode which is previously reported by Warren et al. and Zubkowski et al. [26]. The oxygen atom of protonated acetate group is not involved in coordination with metal ion in this structure, which is present in earlier reported structure. Complex (**I**) has been solved afresh and included for the sake of explanation of its crystal structure, which is different from previously discussed structure.

2. Experimental

2.1. Materials and Physical Measurements

All the starting reagents of analytical grade were used without further purification. The melting points were determined with an electrically heated apparatus. C, H, N elemental analyses were obtained with a CHNS-O analyzer flesh-EA-1112 series. The IR spectra of compounds were recorded on Perkin-ELMER FTIR spectrometer in the range 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) data were collected on a NetzschTG-209 instrument. Single crystal structural X-ray diffraction was carried out on a Bruker Apex-II CCD diffractometer using Mo Kα ($\lambda = 0.71069$) at room temperature. The X-ray powder diffraction (XRPD) measurements were recorded on a Rigaku miniflex II, X-ray diffractometer with Cu Kα radiation.

2.2. Synthesis of {[Co(III)-μ^6-(H-EDTA-κ^5 N1,N2,O2,O6,O8).H_2O].2H_2O} Complex

A mixture of cobalt (III) nitrate (1 mmol, 0.245 g) and EDTA (1 mmol, 0.292 g) were dissolved in de-ionized water and stirred with heating slowly until a clear solution was obtained, then place the solution in conical for growing the crystalline product. Dark pink colored needle like crystals appeared within 2 weeks. M.p. > 300°C. Anal. Calcd for. $C_{10}H_{19}CoN_2O_{11}$ (%): C, 29.85; H, 4.72; N, 6.97; Found: C, 29.67; H, 4.36; N, 6.65. ESI-MS (H_2O): *m/z*: 486.0337[M + 2Na + 1K + 1], 445.1773[M + Na + H_2O + 2], 371.9872[M-3H_2O+Na]. IR (cm^{-1}) selected bonds: IR (cm^{-1}) selected bonds: υ = 3365 (b) (O–H), 3096 (w) (C—H), 1475 (m) $(COO^-)_{asy}$, 1376 (s) $(COO^-)_{sy}$, 1108 (s) (C–O), 946–579 (s) (M–O). (b = broad, m = medium, w = weak, s = strong).

2.3. X-ray Crystallography

The crystals were grown by slow evaporation at room temperature and recrystallized in de-ionized water (Fig. 1). X-ray data of all these complexes were collected on a Bruker's Apex-II CCD diffractometer using Mo Kα ($\lambda = 0.71069$) at room temperature. The data collected by CCD diffractometer were processed by SAINT. Lorentz and polarization effects and empirical absorption corrections were applied using SADABS from Bruker. The

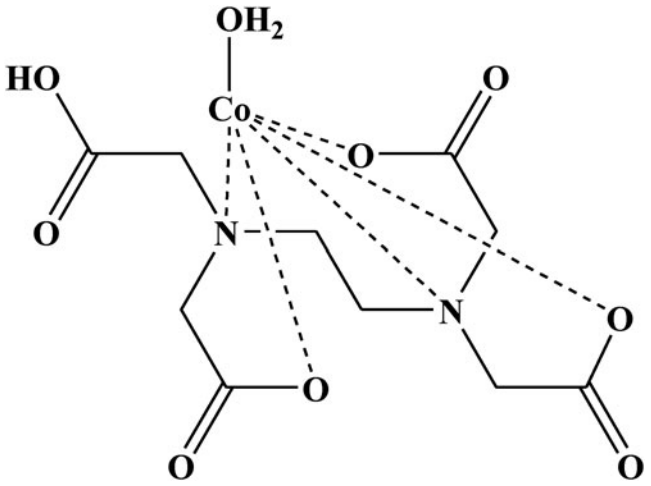

Figure 1. Structure of complex (**I**) showing coordination modes of EDTA (ethylenediamine-*N*,*N*, *N*′,*N*′- tetra acetic acid) with Co^{3+} metal ion.

structure was solved by direct methods, using SIR-92 [27] and refined by full-matrix least squares refinement methods [28] based on F^{-2}, using SHELX-97. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules were located from the difference Fourier synthesis and were refined isotropically with U_{iso} values 1.2 times that of their carrier oxygen atoms, with their distances fixed as 0.82 (2) Å. All other hydrogen atoms were fixed geometrically with their U_{iso} values 1.2 times of methylene carbons. Geometry of this complex and hydrogen bonding interactions were calculated using PARST program [29]. All the drawings of complexes were made using ORTEP [30] and MERCURY [31] programs. All calculations were performed using Wingx package [32].

3. Results

3.1. IR Spectroscopy

As shown in Fig. S1 (Supplementary material), the broad absorption band at 3365 cm^{-1} in complex (**I**) is assigned to the characteristic peaks of O–H vibration. Medium absorption band due to vibrations at 1475 and 1376 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of carboxylate groups, respectively. The peaks observed at 3096 cm^{-1} are in good agreement with C—H vibrations. The presence of peaks in the region of 946–579 cm^{-1} are due to M—O vibrations.

3.2. X-ray Crystal Structure

The X-ray crystallographic analysis shows that there is monomeric Co(III) complex with EDTA (Fig. 2), where cobalt is hexa-coordinated to the nitrogen donors (N1 and N2) and oxygens (O2, O6, and O8) of three acetate groups and one oxygen (O1W) from a water molecule adopts μ^5 octahedral geometry whereas one protonated acetate group of an EDTA ligand is free from any coordination (Fig. 3).

There are two lattice water molecule present in this complex which is showing strong H-bonding interactions with protons of lattice water O2W and O3W (Fig. 4(a)). Oxygen

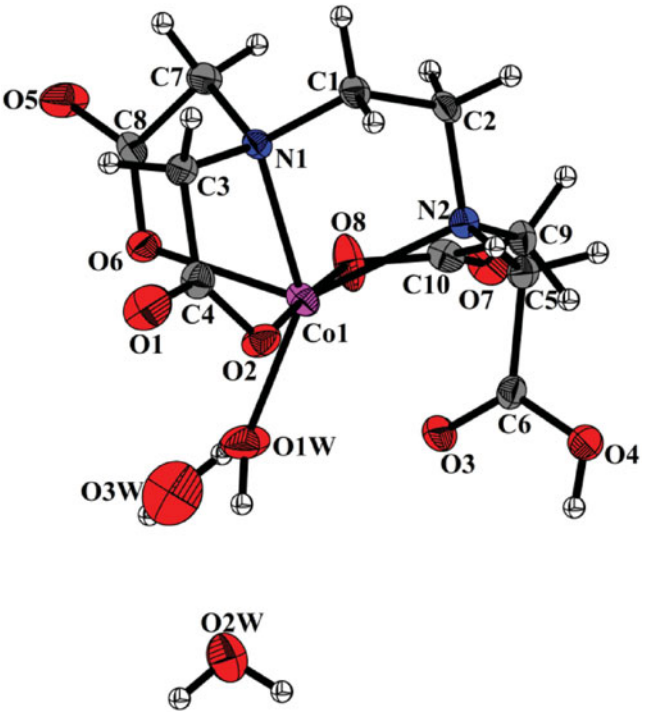

Figure 2. ORTEP diagram showing complexation and bond arrangement of Co^{3+} with EDTA in complex (**I**).

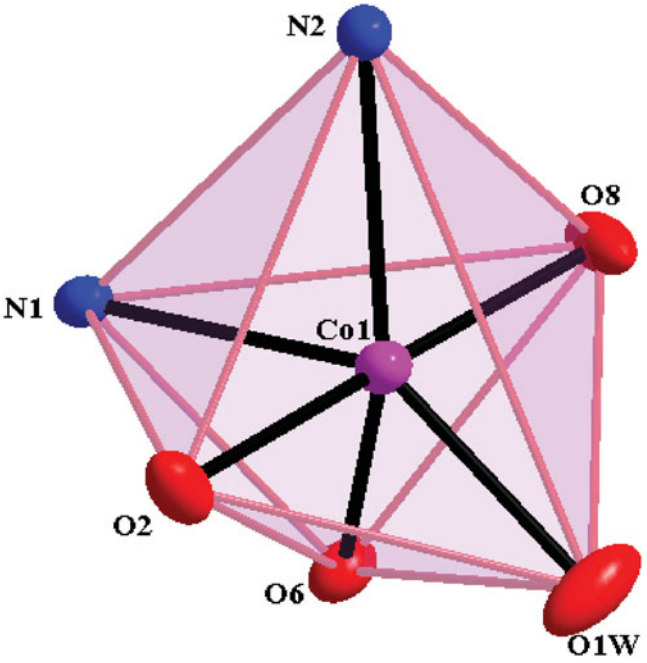

Figure 3. Polyhedral representation showing coordination environment of Co(**III**) with EDTA ligand and coordinated water **O1W** in complex (**I**).

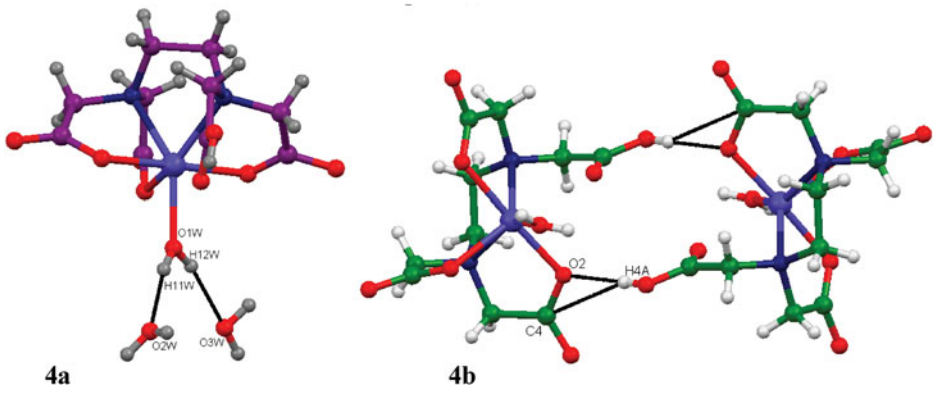

Figure 4. (a) Showing strong H-bonding interactions between of coordinated and lattice water molecules of complex (**I**). (b) The formation of pseudo cavity due to H-bonding interactions of protonated carboxylate hydrogen (H4A) of one basic edta unit with carboxylate oxygen (O2) of another edta unit (where O2-H2A = 1.744 Å, C4-H4A = 2.551 Å).

atoms (O1W) of water molecule occupy the axial position whereas two nitrogen donors, three oxygens of deprotonated acetic acid groups are situated in the pentagonal plane. There formation of pseudo cavity due to H-bonding interactions of protonated carboxylate hydrogen (H4A) of one basic unit of complex (**I**) with carboxylate oxygen (O2) of another present at different symmetry (where O2-H2A = 1.744 Å, C4-H4A = 2.551 Å) (Fig. 4(b)). The Co—O (from carboxylate group) bond lengths lie in the range 2.087–2.284 Å, Co—N (from amine group) bond lengths vary from 2.240 to 2.256 Å, Co—O1W bond length is 2.068 Å. The N—Co—N bond angle is 79.49°, N—Co—O bond angels are in the range of 71.52°–76.30°, O—Co—O bond angels are in the range of 79.14°–102.61°.

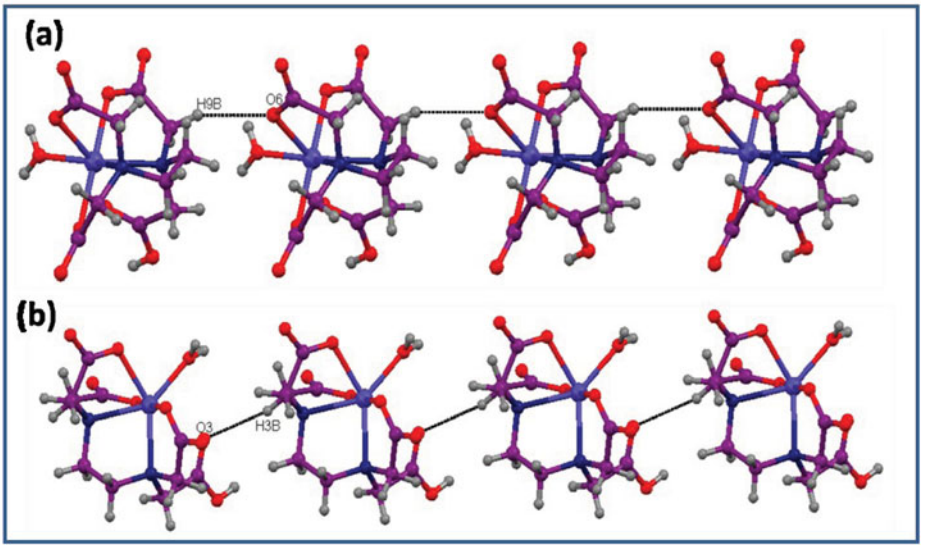

Figure 5. Strong intermolecular H-bonding interactions ((**a**) where O6-H9B = 2.477 Å, along *a*-axis), ((**b**) where O3-H3B = 2.566 Å, along *b*-axis) in complex (**I**).

Table 1. Crystal data and structure refinement for complex (**I**)

Identification code	(**I**)	
Empirical formula	$C_{10}H_{19}CoN_2O_{11}$	
Formula weight	402.20	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	$a = 7.463(5)$ Å	$\alpha = 79.37(3)^\circ$
	$b = 7.791(5)$ Å	$\beta = 82.84(3)^\circ$
	$c = 13.885(8)$ Å	$\gamma = 81.81(3)^\circ$
Volume	781.4(9) Å^3	
Z	2	
Density (calculated)	1.709 Mg/m^3	
Absorption coefficient	1.160 mm^{-1}	
$F(000)$	416	
Crystal size	0.14 × 0.12 × 0.08 mm^3	
Theta range for data collection	1.50°–25.93°	
Index ranges	$-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-16 \leq l \leq 14$	
Reflections collected	8898	
Independent reflections	2993 [R(int) = 0.0574]	
Completeness to theta = 25.93°	97.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.5991	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2993/11/238	
Goodness-of-fit on F^2	1.058	
Final R indices [$I > 2\,\sigma(I)$]	$R1 = 0.0581$, $wR2 = 0.1476$	
R indices (all data)	$R1 = 0.0800$, $wR2 = 0.1604$	
Largest diff. peak and hole	0.901 and −0.541 e Å^{-3}	
CCDC number	**979310**	

The carbon–oxygen distance for the protonated O4 is 1.308 Å, compared to an average of 1.233–1.287 Å for the three other carbon to noncoordinated oxygen bonds. The geometry of the Co (III) complex is significantly distorted away from an octahedral geometry. The coordinated water O1W is hydrogen bonded to both lattice water molecules where H11W-O2W distance is 1.954 Å and H12W-O3W distance is 2.073 Å. Lattice water O3W does not participating further in H-bonding interactions. Lattice water molecule O2W shows strong H-bonding interactions with acetate groups, i.e., H21W and H22W are interactiong with O1 of deprotonated acetate group (where H22W-O1 = 2.010 Å and H21W-O1 = 2.484 Å) and H21W is interacting with O4 of protonated acetate group (where H21W-O4 = 2.703 Å). There are strong intermolecular H-bonding interactions along a-axis and b-axis lead to the formation of 3D crystal structure in complex (**I**) (Fig. 5). By comparing powder

Table 2. Showing important H-bonding interactions in compound (**I**)

X-H . . . Y	X . . . Y	H . . . Y	∠X-H . . . Y
O1W-H11W . . . O2W	2.77	1.96(44)	167
O1W-H12W . . . O3W	2.86	2.07(46)	165
C5-H5A . . . O1[1]	3.70	2.74(4)	171
C1-H1A . . . O1[1]	3.62	2.66(4)	178
C1-H1A . . . O2W[2]	3.27	2.81(4)	110
C2-H2A . . . O5[3]	3.72	2.87(4)	147
C9-H9B . . . O5[3]	3.49	2.85(4)	124
C7-H7B . . . O7[3]	3.56	2.97(3)	121
C2-H2B . . . O6[4]	3.55	2.93(4)	122
C9-H9B . . . O6[4]	3.39	2.48(3)	157
C7-H7B . . . O7[5]	3.54	2.87(3)	126
C3-H3B . . . O3[5]	3.51	2.57(4)	165
C3-H3A . . . O2W[5]	3.29	2.76(5)	115
O2W-H21W . . . O1[6]	3.19	2.49(46)	146
O2W-H21W . . . O4 [7]	3.22	2.70(58)	123
O3W-H31W . . . O5[8]	3.11	2.77(85)	106
O3W-H32W . . . O5[8]	3.11	2.82(74)	103
O2W-H22W . . . O1[8]	2.82	2.01(45)	172
O4-H4A . . . O2[9]	2.53	1.74(44)	158
O4-H4A . . . O3[9]	3.29	2.96(55)	106
O4-H4A . . . O1[9]	3.35	2.75(40)	131
O3W-H31W . . . O3W[10]	3.25	2.96(57)	103
O3W-H31W . . . O7[11]	3.69	2.89(43)	163

Notes. Equivalent positions: (**0**) x, y, z; (**1**) $-x+1, -y+1, -z$; (**2**) $x+1, +y-1, +z$; (**3**) $-x+1, -y+1, -z+1$; (**4**) $x+1, +y, +z$; (**5**) $x, +y-1, +z$; (**6**) $-x, -y+2, -z$; (**7**) $x-1, +y, +z$; (**8**) $x, +y+1, +z$; (**9**) $-x+1, -y+2, -z$; (**10**) $-x, -y+2, -z+1$; (**11**) $-x+1, -y+2, -z+1$.

X-ray diffraction pattern of the complex (**I**), experimental and generated powder patterns are almost identical with respect to the positions and intensities of the diffraction peaks, as shown in Fig. S2. Crystal data and structure refinements for complex (**I**) are given in Table 1, while important H-bonding parameters are given in Table 2. The mass spectrum of complex (**I**) shows great agreements with experimental and X-ray crystal data (Fig. S3). Complete listings of the bond distances, bond angles and torsion angles around Co (III) ions are included in the supplemental material (Tables S4 and S5).

3.3. Thermo Gravimetric Analysis

The TG curve of complex (**I**) is shown in Fig. 6, which shows that the complex is stable up to 80°C and above that loss of two lattice water molecules with resultant weight 91.05% (calcd. 91.51%) and after that loss of one coordinated water molecule up to 120°C (resultant weight 86.4%, calcd. 86.57%). The organic compound stable up to 390°C and after that sharp decomposition of complex starts up to 415°C with resultant weight is 3.85%. The first sharp exothermic peak (12.00 W/g) at 80°C is due to release of two lattice water molecules, the second exothermic peak (15.89 W/g) at 120°C is due to release of one coordinated water

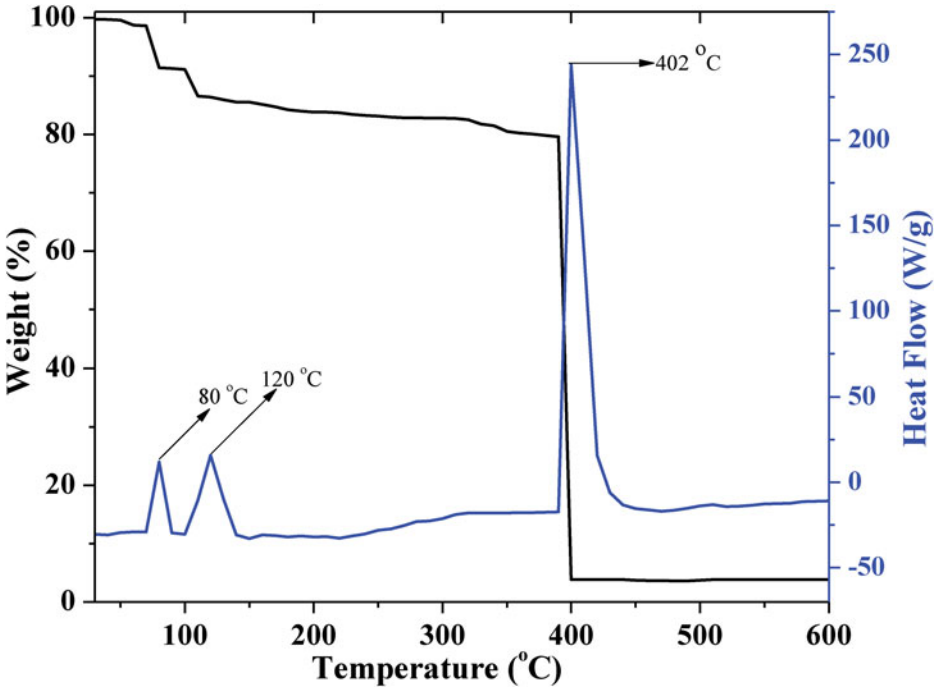

Figure 6. TG-DTA spectrum of complex (**I**).

molecule, and the third sharp peak (243.6 W/g) at 402°C is due to complete decomposition of organic compound along its metal oxides.

4. Conclusion

In summary, we have synthesized a monomeric complex of Co (III) where coordination network based on the EDTA as multidentate ligand. The structural characterization and thermal properties of this complex has been completely described. Complex (**I**) crystallized in triclinic centrosymetric space group with κ^5 coordination modes of EDTA. The complex (**I**) occupied distorted octahedral geometry, where three carboxylate oxygen atoms, two nitrogen atoms, one water molecule O1W are coordinated. There are two lattice water molecules that are present in the molecular structure of complex (**I**) responsible for strong H-bonding interactions and high thermal stability.

Acknowledgment

R. K. Mudsainiyan thanks UGC-BSR for fellowship.

Supplementary Data

Supplemental data for this article can be accessed at www.tandfonline.com/gmcl. IR spectrum of complex (**I**). Comparison of X-RD powder patterns of complex (**I**). Mass spectrum of complex (**I**). Tables of selected bond distances, bond angles and torsion angles. The *cif* and structure factor data are available from Cambridge structure data base, free of cost, CCDC number = **979310**.

References

[1] (a) Zhao, B., *et al.* (2004). *J. Am. Chem. Soc.*, *126*, 15394. (b) Matsuda, R., *et al.* (2004). *J. Am. Chem. Soc.*, *126*, 14063.
[2] (a) Chen, W., *et al.* (2003), *J. Am. Chem. Soc*., *125*, 9266. (b) Li, Y., & Yang, R. T. (2006). *J. Am. Chem. Soc*., *128*, 726.
[3] Stavila, V., Davidovich, R. L., Gulea, A., & Whitmire, K. H. (2006). *Coord. Chem. Rev.*, *250*, 2782.
[4] Hosken, B. D., Cockrill, S. L., & Macfarlane, R. D. (2005). *Anal. Chem.*, *77*, 200.
[5] Wang, C.-C., Yang, C.-H., Lee, C.-H., & Lee, G.-H. (2002). *Inorg. Chem.*, *41*, 429.
[6] Rajput, L., & Biradha, K. (2007). *Cryst. Growth Des.*, *7*, 2376.
[7] Guoqing, Z., Juan, S., & Qiying, J., Kaibai, Y. (2011). *Chin. J. Chem.*, *29*, 2650.
[8] Liu, D.-S., *et al.* (2011). *Inorg. Chim. Acta.*, *376*, 112.
[9] Ragunath, L., & Sivasankar, B. N. (2010). *J. Chem. Crystallogr.*, *40*, 1170.
[10] Xiong, D.-B., Chen, H.-H., Yang, X.-X., & Zhao, J.-T. (2007). *Inorg. Chim. Acta.*, *360*, 1616.
[11] (a) Cui, H.-B., *et al.* (2008). *Angew. Chem. Int. Ed. 47*, 3376. (b) Kong, X.-J., *et al.* (2008). *Angew. Chem. Int. Ed.*, *47*, 2398.
[12] (a) Kou, H.-Z., Jiang, Y.-B., & Cui, A.-L. (2005). *Cryst. Growth Des.*, *5*, 77. (b) Ma, J.-X., Huang, X.-F., Song, Y., Song, X.-Q., & Liu, W.-S. (2009). *Inorg. Chem.*, *48*, 6326.
[13] Kong, X.-J., *et al.* (2010). *Chem. Eur. J.*, *16*, 5292.
[14] Weakliem, H. A., & Hoard, J. L. (1959). *J. Am. Chem. Soc.*, *81*, 549.
[15] McCandlish, E. F. K., Michael, T. K., Neal, J. A., Lingafelter, E. C., & Rose, N. J. (1978). *Inorg. Chem.*, *17*, 1383.
[16] Gomez-Romero, P., Jameson, G. B., Casan-Pastor, N., Coronado, E., & Beltran, D. (1986). *Inorg. Chem.*, *25*, 3171.
[17] Solans, X., Font-Bardia, M., Aguilo, M., Arostegui, M., & Oliva, J. (1987). *Acta Ciyt.*, *C43*, 648.
[18] Fackler, J. P, Jr., Kristine, F. J., Mazany, A. M., Moyer, T. J., & Shephard, R. E. (1985). *Inorg. Chem.*, *24*, 1857.
[19] Lind, M. D., Hoard, J. L., Hamor, M. J., & Hamor, T. A. (1964). *Inorg. Chem.*, *3*, 34.
[20] Richards, S., Pedersen, B., Silverton, J. V., & Hoard, J. L. (1964). *Inorg. Chem.*, *3*, 27.
[21] (a) Smith, G. S., & Hoard, J. L. (1959). *J. Am. Chem. Soc.*, *81*, 556. (b) Coronado, E., *et al.* (1986). *J. Am. Chem. Soc.*, *108*, 900.
[22] Okazaki, H., Tomioka, K., & Yoneda, H. (1983). *Inorg. Chim. Acta.*, *74*, 169.
[23] Stephens, F. S. (1969). *J. Chem. Soc. A.*, 1723.
[24] Hoard, J. L., Kennard, C. H. L., & Smith, G. S. (1963). *Inorg. Chem.*, *2*, 1316.
[25] Kočanová, I., Kuchár, J., Dankovičová, V., & Černák, J. (2010). *Acta Cryst. E*, *66*, m196.
[26] (a) Warren, R. M. L., Haller, K. J., Tatehata, A., & Lappin, A. G. (1994). *Inorg. Chem.*, *33*, 227. (b) Zubkowski, J. D., Perry, D. L., Valente, E. J., & Lotti, S. (1995). *Inorg. Chem.*, *34*, 6409.
[27] Altomare, A., Cascarano, G., Giacovazzo, C., & Guagliardi, A. (1993). *J. Appl. Crystallogr.*, *26*, 343.
[28] Sheldrick, G. M. (2008). *Acta Cryst. A*, *A64*, 112.
[29] Nardelli, M. (1983). *Comput. Chem.*, *7*, 95.
[30] Farrugia, L. J. (1997). *J. Appl. Crystallogr.*, *30*, 565.
[31] Allen, F. H. (2002). *Acta Cryst., B*, *58*, 380.
[32] Farrugia, L. J. (1999). *J. Appl. Cryst.*, *32*, 837.