

Full Length Research Paper

Preparation of Cobalt (III) complexes with trans-1,2-diaminocyclohexane N,N,N',N'-tetra acetatic acid (CDTA) and ethylenediamine tetraacetic acid (EDTA)

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The preparation and isolation of complexes trans 1,2 diaminocyclohexane N, N, N', N'- tetraacetato cobalt (III) [Co(CDTA)] - and ethylenediamine-tetraacetato cobaltate (III) [Co(EDTA)]- by direct oxidation of cobalt (II) with peroxodisulfate ion in the presence of Ag⁺ ion as a catalyst is being reported. The stoichiometry of the complexes has been confirmed through spectroscopic techniques i.e. UV-Visible, Infrared and Atomic Absorption Spectroscopy. The complexes were found to have similar analytical values, further to confirm the procedure the complex of Co (III) EDTA was first prepared, isolated and analyzed to confirm the structural formula, Co (CDTA)- was also studied as comparatively. The approach was set to characterize compounds as expected to have the molecular formula, K[Co(CDTA)] - xH₂O in crystal form and [Co(CDTA)]- in ionic form.

Key words: Isolated complexes, redox reactions, infrared (IR) spectroscopy, peroxodisulfate protonation.

INTRODUCTION

The nature and the number of bonding sites in multidentate ligands is one of the most interesting and important aspect of present day coordination chemistry. Woodruff et al. (1973) have worked on the structures of metal-EDTA complexes in the solid state and have tried to produce some answers but they could not render to the structures of the metal complexes in aqueous solution. The problem has been carefully considered by Chisholm and Clark (1973) and concluded that the substantial number of EDTA complexes of bivalent metals contained quinquedentate ligand that is, could be represented by MEDTA[H₂O]²⁻ with one uncoordinated carboxylate group. Jolley et al. (1992) studies support for this idea comes from the observation of a common pk value for these complexes which is related to protonation of the free carboxylate group rather than involving any breakage of a metal-carboxylate bond. Offsetting this

argument is the study of Nobuyuki and Hirosin (1965), which confirmed that definite spectral changes accompany the protonation of the copper(II) and cobalt(II) complexes and this is more easily rationalized in terms of at least some six coordinated EDTA compound.

Micheal and Robert (1992) studied the interaction of multidentate cobalt (II)-chelate complexes with ferricyanide ion. According to them, a cyanide-bridge that is, intermediate bridge is formed between CoCyDTA²⁻ and Fe(CN)₆³⁻ in a manner exactly analogous to that for the CoEDTA²⁻ - Fe(CN)₆³⁻ reaction. CyDTA was chosen because the stereochemistry of the cyclohexyl ring plays an important part in reactions of complex of this ligand as reported by Sivaswaroop et al. (1991). Number of inner-sphere reactions involving cyano bridging have been reported by Loussouarn et al. (1992). In such kind of reactions, when at least one of the product ions is

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substitutional labile, the decomposition (or dissociation) of the successor binuclear complex is rapid and conclusion concerning the structure and reactivity of that species must be drawn from indirect evidence as reported by Suzuko et al. (1991).

The self exchange of Co (II) and Co (III) EDTA complexes was first studied by Adamson and Vorres (1956) at pH 2.0 using a 60°C tracer. Schneider and Sheldrick (2002) described an experiment for the light induced electron transferred reaction between $[\text{Co}(\text{EDTA})]^{2-}$ and $\text{S}_2\text{O}_8^{2-}$ by employing $[\text{Ru}(\text{bpy})_3]^{2+}$ as a photocatalyst, but this reaction hardly proceed in the absence of $[\text{Ru}(\text{bpy})_3]^{2+}$. Number of other studies have been undertaken related to complex reaction of EDTA and CDTA complexing agents (Wilkins and Yelin, 1967; Nishida and Kimura, 1987; Albert and Wilkinson, 1970; Ohashi and Yamamoto, 1977; Nakamoto, 1978; Marr and Rocckett, 1972; Fornaro and Coichev, 1999; Turlyan and Kohen, 1995; Horacio and Coichev, 2006). Present study reveals the structure of cobalt (III) complexes and their ratios verification through different spectral techniques.

MATERIALS AND METHODS

Chemicals

Cobalt sulfate, Potassium Peroxodisulfate, Silver Nitrate, Ethylenediamine tetraacetic acid -EDTA, Trans-1,2-Diaminocyclohexane-CDTA N,N,N',N'-tetraacetic acid, Sodium Chloride, Ethyl Alcohol, Cobalt(II) Chloride. All the chemicals were of the analytical grade.

Apparatus and instrumentation

Spectrophotometric techniques were used for the element detection in complex. All types of glass wares, flask, beaker, pipette, cylinder etc used were made up of Pyrex and good quality from SCHOTT DURAN. Iron Magnet heater was of IKAMAG_RTC. Double distilled deionized water and oven having CSW-300 system was used. Balance (Analytical Balance) was of mettler HIOT. Shimadzu UV-Visible Spectrophotometer (type 160 A) was used for determination of cobalt (III). Atomic absorption Spectrometer (model Shimadzu) was used for the determination of elements present in the organic part of complex, that is, carbon, hydrogen, nitrogen and oxygen.

Preparation of reagents

Solutions preparation was done in deionized water. The reagent cobalt (II) sulfate, peroxydisulfate, silver nitrate and ligands (that is, CDTA or EDTA) were mixed in solid form and then dissolved in deionized water to get a clear colored solution by help of magnet stirrer and a little heat. Standard solution of cobalt for atomic absorption spectroscopy measurement, of cobalt (II) having 1000 ppm concentration was prepared by dissolving an appropriate amount of cobalt (II) chloride in measuring flask with deionized water and making up to the mark. Three standard solutions pertaining to concentrations of 1, 2, and 3 ppm were prepared from stock solution cobalt (II) chloride. To establish a concentration of cobalt solution to 400 ppm, calculated amount of compound was

dissolved and made up to the mark with deionized water to prepare the solution of concentration beyond 3.5 ppm. The stock solution was diluted to 200 times.

Methodology

0.01 moles of cobalt (II) sulfate, 0.012 moles of ligands (that is, CDTA and EDTA), 0.003 moles silver nitrate and 0.05 moles of potassium peroxodisulfate were dissolved in accurately measured 80 ml of deionized distilled water at room temperature. The dissolution was facilitated using some heat with stirring to get a clear violet-pink solution. Reaction mixture was kept in water bath between temperatures from 85 to 90°C, while stirring for about two hours such that all peroxodisulfate got decomposed. The color of solution was changed from pink to reddish brown. 0.003 moles of sodium chloride was added to hot solution, to remove silver ion as silver chloride. Then the solution was cooled and filtered and that of total volume of filtrate was about 70 cm³. Ethyl alcohol was added to the filtrate in the same volume and it was kept in controlled temperature for overnight to precipitate out and these precipitate were dried to in oven to crystallization. On the very next day reaction mixture was filtered to isolate the pink precipitate which was washed with excess amount of alcohol, re-crystallization was followed by drying in oven at temperature $\geq 90^\circ\text{C}$.

Analysis

Determination of cobalt

Cobalt (III) complex was examined on Shimadzu 160A UV visible spectrophotometer. The value of λ_{max} was calculated with in two different ranges of 200 to 800 nm and at of 300 to 650 nm to observe the wavelength in which the absorbance is maximum. Different maximum absorbances were observed at 380 and 540 nm. Quantitative determination of cobalt element was analyzed by 2380 Perkin – Elmer Atomic Absorption Spectrophotometer. Hollow cathod lamp of Co⁵⁹ and Air-Acetylene flame (air as oxidant and acetylene as a fuel) were applied and the wavelength was adjusted on 240.7 nm to obtain the maximum absorbance reading for cobalt. Stock solution (containing 1.658 g of complex) was prepared as of unknown solution, three standard solutions of cobalt(II) chloride contain 1, 2 and 3 ppm cobalt were prepared to get linear baseline graph of absorbance vs. concentration as the standard procedure as shown. The observations and the graph are shown in Table 1 and Figure 1 respectively.

Elemental analysis of organic part of the molecule

To characterize the structure of the compound, it was analyzed by infrared spectrophotometer. The previous reports have suggest that the method of Nujol mull sampling method for compound. Instead alkali halide disk, spectra was obtained with KBr pellets.

RESULTS AND DISCUSSION

The preparation and isolation were carried out as described in experimental conditions. The crystal pink chloride compounds were isolated and identified by spectroscopic techniques. Spectrophotometric analysis show two different λ_{max} for cobalt III in the UV visible range at 380 and 540 nm as have shown in the Tables 2 and 3 and Figures 2 to 7. The silver catalyzed, direct

Table 1. Atomic Absorption Spectroscopic Data for Co-CDTA.

Solutions	Concentration in ppm	Absorbance
Standard No. 1	1	0.0060
Standard No. 2	2	0.0120
Standard No. 3	3	0.0170
Standard No. 4	x	0.0015

The amount of cobalt = $X \times 50 / 100 \times 100 / 2.5 \times 500 / 1000 = \text{mg}$, the unknown concentration 'X' from the graph is 1.925 mg per liter.

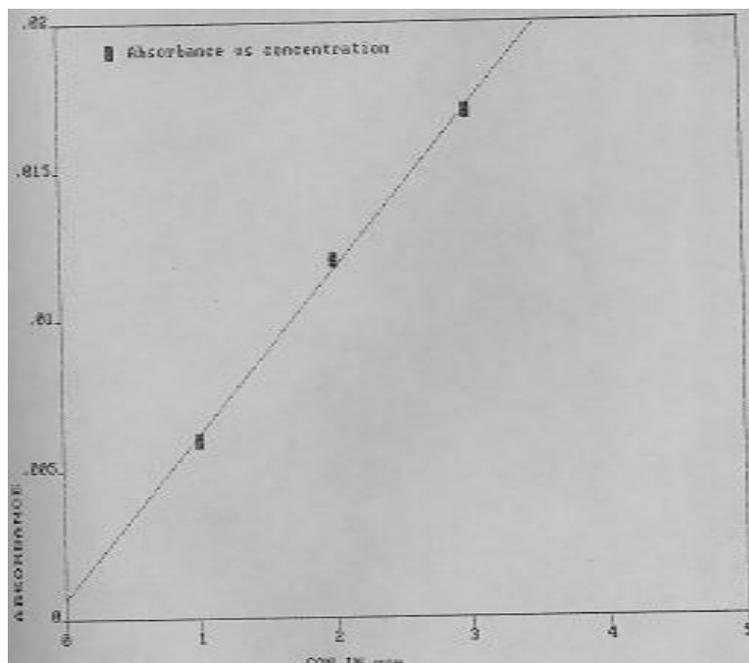


Figure 1. CoCDTA graph of concentration vs. absorbance by Atomic Absorption Spectroscopy, the regression of polynomial line $(6.667\text{E-}04) + (5.500\text{E-}03) \times x$.

oxidation of cobalt II by peroxodisulfate to prepare $[\text{Co}(\text{III})\text{CDTA}]^-$ complex has been studied. The prepared and isolated complexes are expected to contain cobalt metal and other components as carbon, hydrogen, nitrogen and oxygen. The stoichiometry of the complex has been confirmed through spectroscopic techniques that is, UV-Visible, infrared and atomic absorption spectroscopy. Complex was found to have similar analytical values as reported. To understand more and confirm the procedure the complex of Co (III)-EDTA was first prepared and isolated and analyzed to confirm the structure formula, as shown in Figures 6 and 7.

The $[\text{Co}(\text{CDTA})]^-$ was then studied the same manner as $[\text{Co}(\text{EDTA})]^-$ complex. Elemental analysis for the value of cobalt was estimated to have the same % value as reported before. Accordingly the compound is expected to have the molecular formula, $\text{K}[\text{Co}(\text{CDTA})]-$

$x\text{H}_2\text{O}$ in crystal form and $[\text{Co}(\text{CDTA})]^-$ in ionic form (in solution form). The molecular formula of $\text{K}[\text{Co}(\text{CDTA})]-x\text{H}_2\text{O}$ is supposed to be correct, having one hexadentate ligand bonded to one central Co atom $[\text{CoO}(\text{CH}_2)_4\text{N}(\text{CH}_2\text{COO})_2]^-$. The number of hydrated molecules of water is supposed to be more probably two than one molecule. The presence of three molecules of water in the hydrated molecule is not supported by our results as discussed below.

If $x = 1$ (one molecule of water), the molecular weight of $\text{K}[\text{Co}(\text{CDTA})], \text{H}_2\text{O}$ will be 458.35 g/ mole.

Thus the expected percentage of cobalt content would be 12.86%. If number of water molecules present in the hydrated form of complex is two, $x = 2$, the molecular weight of $\text{K}[\text{Co}(\text{CDTA}), \text{H}_2\text{O}]$ would be 476.38, in which

Table 2. UV –Visible Data of Absorption of CoCDTA in Filtrate and ppt.

<i>CoCDTA in Filtrate</i>				<i>CoCDTA in ppt</i>			
λ	ABS	λ	ABS	λ	ABS	λ	ABS
650	0.038	640	0.048	650	0.022	640	0.033
630	0.065	620	0.089	630	0.051	620	0.079
610	0.122	600	0.165	610	0.118	600	0.167
590	0.214	580	0.268	590	0.222	580	0.280
570	0.321	560	0.369	570	0.335	560	0.378
550	0.411	540	0.440	550	0.407	540	0.419
530	0.453	520	0.440	530	0.412	520	0.383
510	0.403	500	0.349	510	0.338	500	0.281
490	0.290	480	0.236	490	0.223	480	0.169
470	0.192	460	0.157	470	0.126	460	0.097
450	0.130	440	0.116	450	0.081	440	0.081
430	0.120	420	0.144	430	0.097	420	0.133
410	0.190	400	0.257	410	0.191	400	0.268
390	0.321	380	0.347	390	0.344	380	0.375
370	0.328	360	0.289	370	0.352	360	0.307
350	0.261	340	0.264	350	0.271	340	0.278
330	0.331	320	0.506	330	0.350	320	0.553
310	0.931	300	1.766	310	1.013	300	1.946

Table 3. UV –Visible data of absorption of CoEDTA in filtrate and ppt.

<i>CoEDTA in filtrate</i>				<i>CoEDTA in ppt</i>			
λ	ABS	λ	ABS	λ	ABS	λ	ABS
600	0.172	590	0.221	600	0.188	590	0.248
580	0.275	570	0.327	580	0.314	570	0.383
560	0.376	550	0.419	560	0.449	550	0.510
54	0.449	530	0.464	54	0.559	530	0.590
520	0.453	510	0.419	520	0.583	510	0.542
500	0.367	490	0.308	500	0.472	490	0.391
480	0.254	470	0.210	480	0.319	470	0.256
460	0.174	450	0.148	460	0.205	450	0.158
440	0.133	430	0.141	440	0.127	430	0.118
420	0.171	410	0.222	420	0.138	410	0.183
400	0.293	390	0.368	400	0.254	390	0.320
380	0.406	370	0.391	380	0.340	370	0.304
360	0.351	350	0.310	360	0.242	350	0.185
340	0.297	330	0.339	340	0.167	330	0.218
320	0.486	310	0.853	320	0.398	310	0.856
300	1.636			300	1.829		

the expected percentage of cobalt contents are to be 12.37%. In the case of $x = 3$ the molecular weight of $K [Co (CDTA)], 2H_2O$ be 476.38 and the expected percentage of cobalt content would be 11.92% as in Table 4.

In the present study the data pertains to the 12.28% of cobalt present in complex. This leads to believe that a molecular formula with two of hydrated water molecules in the coordination sphere of the complex is correct, and also presence of one K^+ ion in the crystal form of the

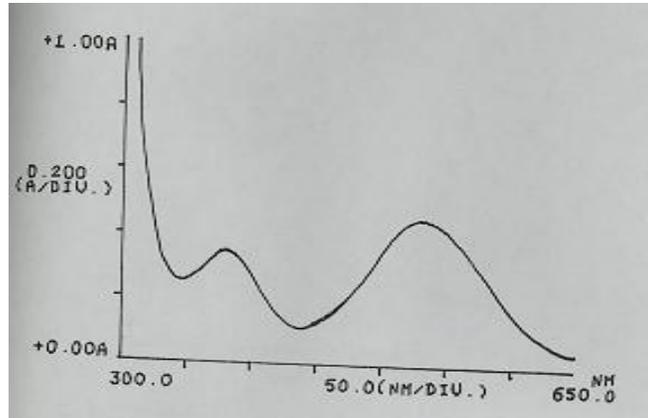


Figure 2. Graph show absorbance vs. wavelength (λ) nm for CoCDTA in filtrate.

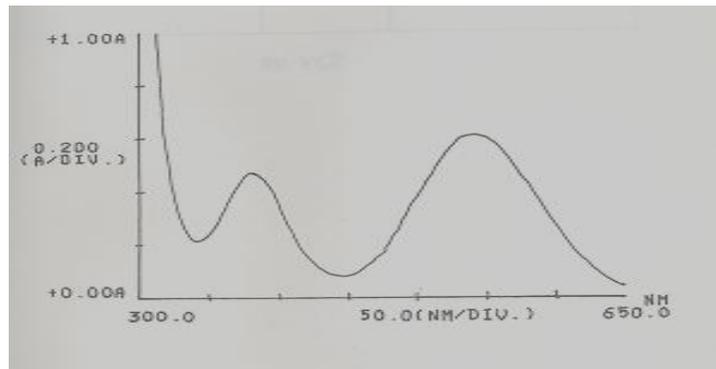


Figure 3. Graph shows plot of absorbance vs. wavelength (λ) nm for CoCDTA in ppt.

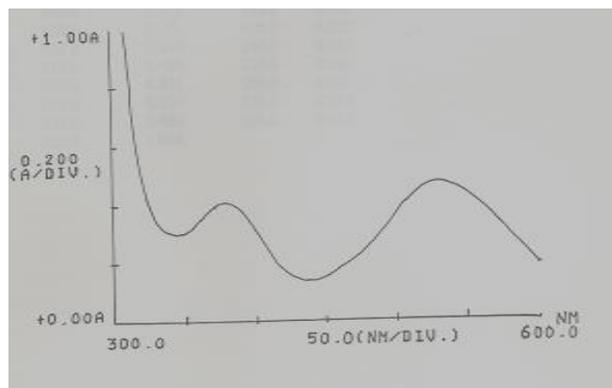


Figure 4. Graph shows plot of absorbance vs. wavelength (λ) nm for CoEDTA in filtrate.

compound is substantial, therefore the proposed molecular formula for the complex of cobalt (III) with

CDTA is $K [Co (CDTA), 2H_2O]$ where-as the complex of cobalt (III) with EDTA is $K [Co \{EDTA\}2H_2O]$.

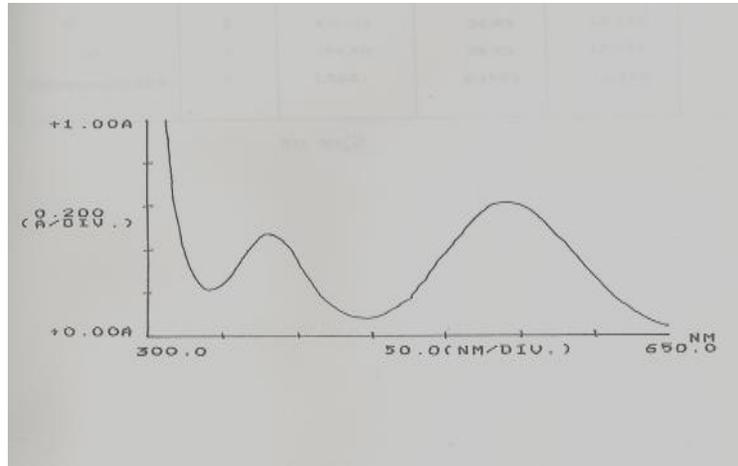


Figure 5. Graph shows plot of absorbance vs. wavelength (λ) nm for CoEDTA in ppt.

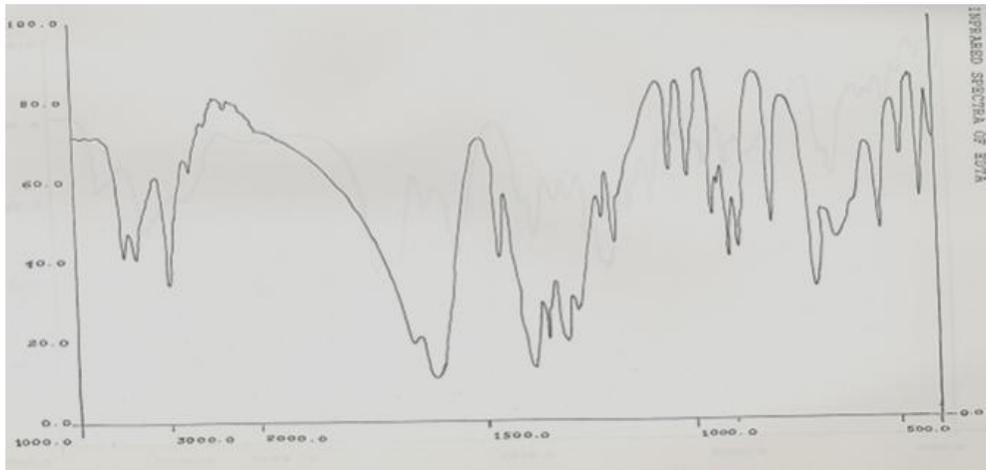


Figure 6. Infrared spectra of EDTA.

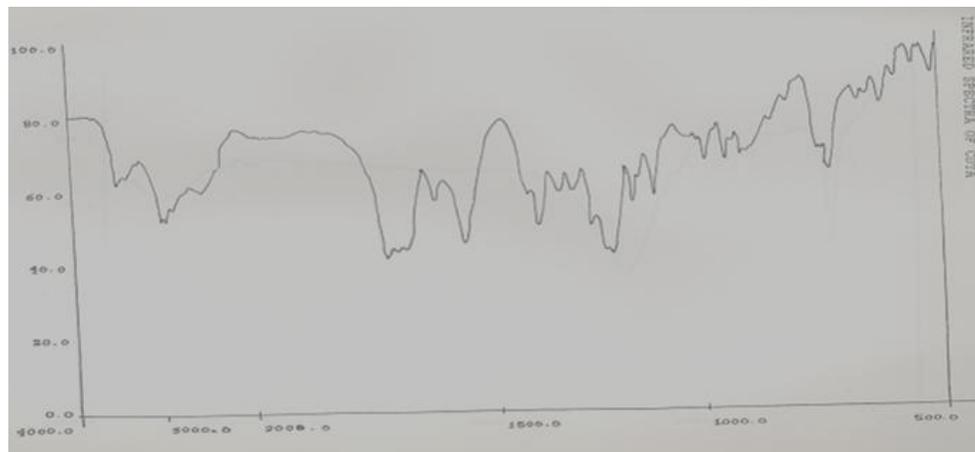


Figure 7. Infrared spectra of CDTA.

Table 4. Percentage of Cobalt in Complex Theoretically and Experimentally Supposed to have Molecular Formula $K [Co (CDTA)] xH_2O$, So $x \leq 2$.

Method	X Molecules	Wt. of complex (g)	Wt of Cobalt (g)	Percentage of Cobalt
Theoretically	1	458.35	58.93	12.86
Theoretically	2	476.38	58.93	12.73
Theoretically	3	494.40	58.93	12.92
Experimentally	x	1.568	0.1925	12.28

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REFERENCES

- Albert FC, Wilkinson C (1970). The element of the first transition series. *Advanced Inorganic Chemistry*, FR.S, 3rd Ed. 877-878.
- Chisholm MH, Clark HC (1973). Cationic acetylenic platinum (II) compounds and their derivatives. V. Comparative study with π -olefinic complexes. *Inorg. Chem.* 12(5):998-1008.
- Fornaro A, Coichev N (1999). Iron (III) complex- catalyzed reduction of Tris (Oxalato) cobaltate (III) by L-Ascorbic acid. *J. Coord. Chem.* 46:519-525.
- Horacio M, Coichev N (2006). Kinetic studies of the oxidation of L-ascorbic acid by tris (oxalate) cobaltate in the presence of CDTA metal ion complexes. *J. Braz. Chem. Soc.* 17:364-368.
- Jolley WH, Stranks DR, Swaddle TW (1992). Kinetics of the aqueous cobalt (II)/cobalt (III)/EDTA system at variable pressure. *Inorg Chem.* 31:507.
- Loussouarn A, Ouadi A, Morandeau L, Remaud P, Giles P, Gestin JF, Webb J (1992). Synthesis of new semi rigid agents of Samarium-153. *Tetrahedron Letts.* 44:3539.
- Marr G, Rocckett BW (1972). *Practical Inorganic Chemistry*, 1st Ed Van Nostrand Reinhold London. 25-26:147-149.
- Micheal DJ, Robert JB (1992). Kinetics and mechanism of metal ion substitution on a cobalt (III) complex containing a pendant phenanthroline. *Inorg. Chem.* 31:808 -815.
- Nakamoto K (1978) *Infrared and Raman Spectroscopy of Inorganic and Coordinated Compounds*, 2 Ed John Wiley of Sons N.Y; New York, P. 313.
- Nishida S, Kimura M (1987). Light induced electron transfer reactions, kinetics of the oxidation of EDTA Cobaltate(II) complexes by peroxodisulphate ion, induced by irradiation with visible light of aqueous solution containing trans-2,2' bipyridine-ruthenium(II) ion. *Bull. Chem. Soc. Jpn.* 60:2367.
- Nobuyuki T, Hirosin O (1965). Stability constant of some substitution inert cobalt (III) complexes. *Bull. Chem. Soc. Jpn.* 38:1054.
- Ohashi K, Yamamoto K (1977). The Silver (I) ion catalyzed oxidation of EDTA cobaltate (III) by the peroxodisulfate ion. *Bull. Chem. Soc. Jpn.* 50:3049.
- Schneider TR, Sheldrick GM (2002). Substructure solution with *SHELX*. *Acta Crystallogr. Sect. D.* 58:1772.
- Sivaswaroop P, Kumar KA, Rao PVK (1991). Oxidation of Trans 1,2 Cyclohexanediaminetetraacetate cobalt (III) by peroxodisulphate catalyzed by Ag(I) in Acetate buffer. *Bull. Chem. Soc. Jpn.* 64: 641-666.
- Suzuko YN, Aiko N, Noriko M, Masaru K (1991). Kinetic Study on the quenching of the photo excited $[Ru(bipy)_3]^{2+}$ with $[Co(EDTA)]^-$ in the presence of EDTA, CDTA and $C_2O_4^{2-}$. *Bull. Chem. Soc. Jpn.* 64:1866-1875.
- Tur'yan Y, Kohen R (1995). Formal redox potentials of the dehydro-L-ascorbic acid/L-ascorbic acid system. *J. Electro. Anal. Chem.* 380:273-282.
- Wilkins RG, Yelin R (1967). Kinetics evidence pertaining to the structure of the cobalt (II) Ethylenediaminetetraacetate (EDTA) complex in aqueous solution. *J. Am. Chem. Soc. Jpn.* 89:5497.
- Woodruff WH, Margerum DW, Milano MJ, Pardue HL, Santini RE (1973). Kinetics and mechanism of the oxidation of cobalt (II) aminopolycarboxylate complexes by hypobromous acid and hypobromite ion. *Inorg. Chem.* 12:1498 -1501.