Asian Journal of Chemistry Vol. 9, No. 4 (1997), 681–691

Confirmation of Structure, Geometry and Symmetry of $[Co(EDTA)]^-$ Ion by Determining Force Constants

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A simplified procedure was proposed by the authors for the synthesis of sodium ethylenediaminetetraacetate cobaltate(III). Adopting the structural parameters from the data presented by Weakliem and Hoard, force constants were evaluated for the complex ion $[Co(EDTA)]^-$. The data were compared with the force constants reported for similar complex ions. However discrepancies were observed for some bonds such as Co—N in two different environments. A possible explanation was offered by the authors to confirm the octahedral structure of $[Co(EDTA)]^-$ ion.

INTRODUCTION

Coordination complexes of cobalt(III) are numerous and diversity is observed in several aspects, such as coordination number, oxidation state, stereochemistry, lability and stability.[1] The structural integrity of these complexes is due to formation of covalent bonds.

Ethylenediaminetetraacetic acid, EDTA, containing four dissociable protons, is a neutral acid[2] and its anion forms stable complexes due to several factors, such as formation of stable five-membered rings with the central metal atom.

Vibrational spectroscopy is useful in characterizing both organic and inorganic compounds and it is applied in the investigation of the nature of inter and intramolecular forces, the identification and confirmation of functional groups and the determination of molecular symmetries. Hence, investigation on the vibrational spectra of a polyatomic molecule may throw light on its molecular characteristics. Literature survey[3, 4] has revealed that it is possible to correlate the characteristics of a chemical bond with the vibrational parameters. Infrared and Raman spectral data are useful to elucidate the structure, geometry and symmetry of a molecule.

Force constant is defined as the restoring force existing between the two vibrating nuclei in a molecule per unit displacement and it is evaluated using Wilson's F–G matrix method. The magnitude of force constant depends mainly on two factors, *viz.*, bond order and masses of two atoms forming the bond.

EXPERIMENTAL

All chemicals, used in the present investigation, were of Analytical Reagent grade. The complex was prepared by following the method reported by Ogino and Ogino.[6] A simplified procedure was also reported by the authors. An aqueous solution of cobalt(II) chloride was mixed with an aqueous solution of disodium salt of ethylenediamine tetraacetic acid in a conical flask, and it was kept in an ice bath. A ten volume hydrogen peroxide solution was added in drops. After the completion of the addition of hydrogen peroxide solution, acetone was added. Reddish-violet crystals separated. They were collected and purified. It was observed, based on spectral measurements, that the sample obtained from the two different procedures are identical.

The ultraviolet-visible absorption spectrum was recorded in a 5501 Cecil spectrophotometer using a 10 mm path-length quartz cell. The infrared spectrum was recorded on Shimadzu 408 infrared spectrometer in the range 4000–200 cm^{-1} and potassium bromide pellet technique was followed. The FTIR spectrum was recorded on Bruker IFS-66V in the range 4000–400 cm^{-1}. The Raman spectrum was recorded in the range 4000–20 cm^{-1} on Dilor Z-24 Spectrometer.

RESULTS AND DISCUSSION

It has been reported[7] that the spectrum of $[Co(EDTA)^-]$ ion shows two ligand field bands at 380 and 535 nm with ε values 140 and 270 mol^{-1} dm^3 cm^{-1} respectively. The specturm of the same ion (Fig. 1) prepared by a simplified procedure, proposed by the authors, shows two ligand bands at 382 and 537 nm with ε values 143 and 268 mol^{-1} dm^3 cm^{-1} respectively which is in good agreement with the previously reported values. Further, the spectrum (Fig. 2) shows one charge-transfer band at 226 nm with ε value 10.885 mol^{-1} dm^3 cm^{-1} which is also in good agreement with the reported value[7] of 225 nm with ε value of 11.000 mol^{-1}dm^{3}cm^{-1}. The Raman spectum is shown in Fig. 8

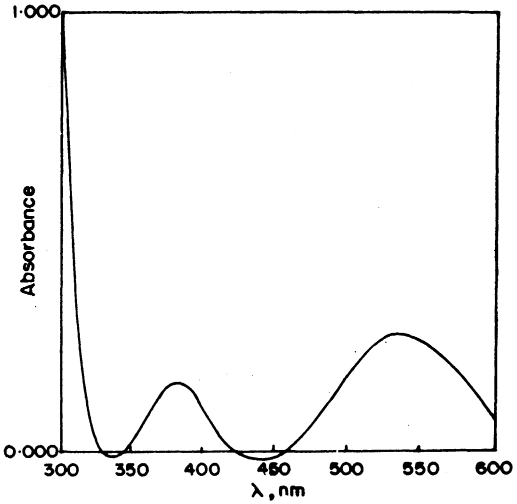

Fig. 1 Ultraviolet-visible absorption spectra of Na[Co(EDTA)] in water in the region 300–600 nm.

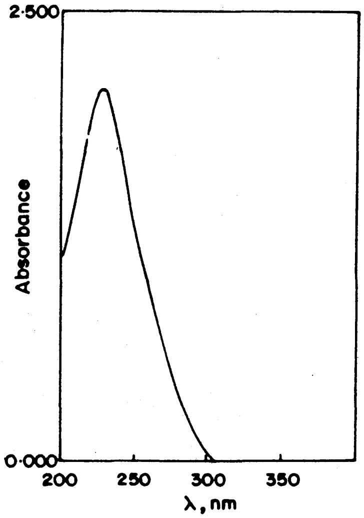

Fig. 2 Ultraviolet absorption spectrum of Na[Co(EDTA)] in the region 200–350 nm.

The ligand, ethylenediaminetetraacetate, acts as a sesquidentate ligand. The existence of a complex with this ligand has been evidenced by the synthesis[8] of Na[Co(EDTA)]. Weakliem and Hoard[5] have made X-ray study on the orthorhombic crystals of $NH_4[Co(EDTA)]\cdot 2H_2O$ and $Rb[Co(EDTA)]\cdot 2H_2O$. Fig. 3 represents[5] electron density in ammonium ethylenediaminetetra- acetatocobaltate(III)dihydrate, projected onto 100 plane and the Fig. 4 represents[5] the model in the perspective of the complex ion. The central metal atom is bonded to two nitrogen atoms which occupy the *cis* positions of an octahedron. Further, it is bonded to one oxygen atom from each of the four CH_2COO^- arms of the ligand. The plane containing the cobalt atom and the two nitrogen atoms is designated as NNM plane. The oxygen atoms, O_5 and O_7, lie opposite to the nitrogen atoms, N_2 and N_1 respectively.

The complex ion carries five five-membered chelate rings and out of them three combine to form a girdle, whereas the other two rings are virtually flat. The girdle lies very close to the NNM plane and the other two rings are perpendicular to this plane. The line bisecting $N_1\hat{Co}N_2$ and $O_5\hat{Co}O_7$ represents the two-fold axis of symmetry and it causes the classification of the five five-memebered rings into three types, *viz.*, one E, two G and two R rings as shown in Fig. 5.

The structural parameters are adopted from the data presented by Weakliem and Hoard.[5] The molecular model, the numbering of the atoms. the orientation of Cartesian coordinates and the internal coordinates are shown in Figs. 5–7. The irreducible representations yield 45 genuine vibrations. The vector method was followed to construct orthonormal set of symmetry coordinates. The Cartesian coordinates were evaluated with the computer program CART and the B matrix was computed using GMAT program. The unsymmetrized and the symmetrized matrices were evaluated. Approximate force constants were assumed or transfer-

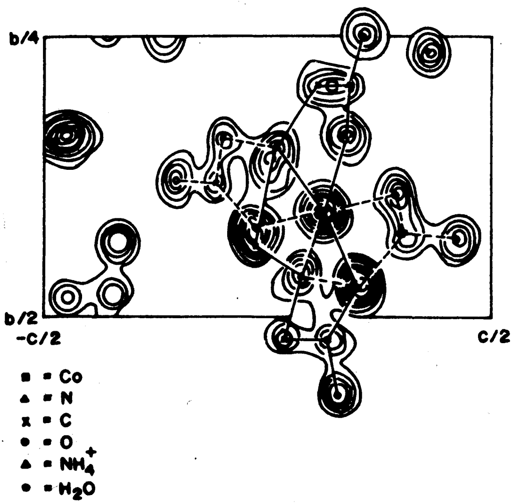

Fig. 3 Electron density in $NH_4[Co(EDTA)]\cdot 2H_2O$ projected onto (IOO) plane

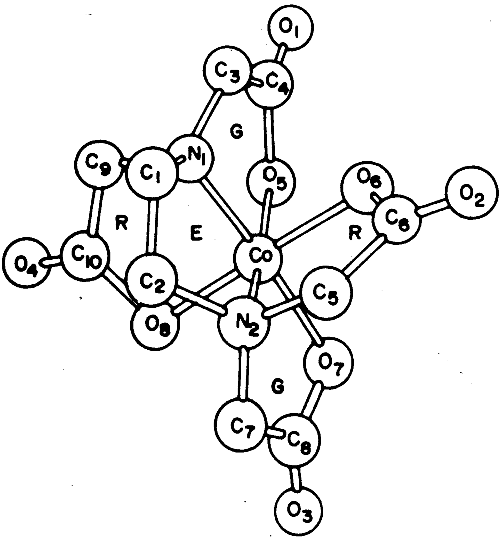

Fig. 4 Model in true perspective of $[Co(EDTA)]^-$

red from molecules having similar environment. The symmetized F matrix was given as input data to solve the secular equation $|FG—E\lambda| = 0$, so as to evaluate λ and these λ values were then compared with the observed values until a very close agreement was obtained. The calculated and the observed values of λ are given in Tables 1 and 2 and the evaluated force constants are given subsequently in Tables 3 and 4. In these tables, some force constants, such as bond-bond interaction force constants are not given, because they are found to be too small.

Since the complex ion, $[Co(EDTA)]^-$, has two nearly identical G–E and R

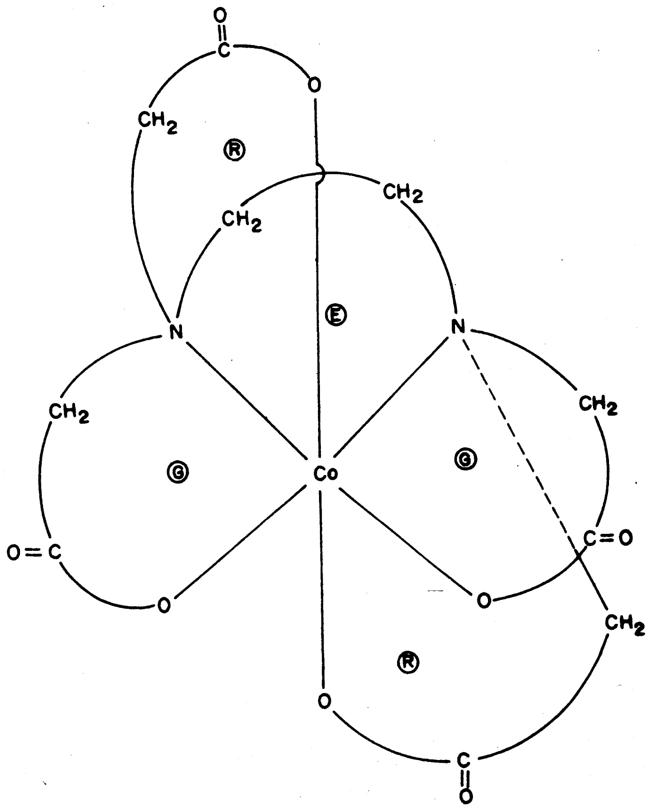

Fig. 5 Molecular model of [Co(EDTA)]⁻ ion (G, E, R rings)

rings, the mean force constants were determined. The two Co—O stretching force constants in the G–E rings are found to be 1.998 and 1.872 mdynÅ^{-1} and those in the R rings are 1.983 and 2.012 mdynÅ^{-1}. The mean Co—O stretching force constants in the G–E rings and in the R rings are 1.935 and 1.998 mdynÅ^{-1} respectively.

Mikami *et al.*[9] have prepared complexes of the ligand, acetylacetato, with transition metals and determined force constants for various bonds. In this paper,[9] they reported the Co—O stretching froce constant as 1.95 mdynÅ^{-1}, based on a complete normal coordinate analysis of the complex. [Co(acac)$_3$]. Thus, the calculated values of force constant of Co—O bond in the present investigation are in good agreement with those reported by Mikami *et al.*[9]

The stretching force constants of the Co—N bond in the G–E rings are found to be 1.342 and 1.690 mdynÅ^{-1} and their mean value is 1.516 mdynÅ^{-1}. Similarly, the stretching force constants in the R rings are found to be 1.099 and 1.035 mdynÅ^{-1} and their mean is 1.067 mdynÅ^{-1}. These data reveal that the Co—N bond in the G–E rings is stronger than that in the R rings.

TABLE-1
OBSERVED AND CALCULATED FREQUENDIES AND THEIR ASSIGNMENTS FOR [Co(EDTA)]$^-$ ION (G–E RINGS)

S. No.	ν_{Obs} cm^{-1} Infrared	Raman	ν_{Cal}, cm^{-1}	Assignment
1.	3463.2	—	—	O—H stretching (hydrates)
2.	—	3437.7	—	O—H stretching (hydrates)
3.	—	3391.2	—	O—H stretching (hydrates)
4.	—	3138.9	—	O—H stretching (hydrates)
5.	2989.1	—	—	C—H asymmetric stretching
6.	—	2753.7	—	C—H symmetric stretching
7.	—	1674.8	—	ionized and coordinated Co—O stretching
8.	1473.3	—	—	ionized and coordinated Co—O stretching
9.	1435.2	1432.4	1424.9	C—C stretching
10.	1370.2	—	1358.7	C—O stretching

TABLE-2
OBSERVED AND CALCULATED FREQUENCIES AND THEIR ASSIGNMENTS FOR [Co(EDTA)]$^-$ ION (R RING)

S. No	ν_{Obs} (cm^{-1}) Infrared	Raman	ν_{Cal} (cm^{-1})	Assignment
1.	—	2637.6	2613.6	asymmetric C—H stretching
2.	—	2574.5	2554.3	symmetric C—H stretching
3.	1647.2	—	1611.5	ionized and coordianted Co—O stretching
4.	—	1336.1	1329.7	C—C stretching
5.	1314.9	—	1304.9	C—C stretching
6.	1157.9	—	1131.7	C—O stretching
7.	1097.2	—	1054.1	C—N stretching
8.	1072.4	—	1061.7	C—N stretching
9.	996.2	—	998.3	N—Co—N stretching
10.	935.7	—	922.4	O—CO—CH_2—N asymmetric stretching
11.	847.2	—	838.9	O—CO—CH_2—N symmetric stretching

TABLE-3

FORCE CONSTANTS[a] OF [Co(EDTA)]$^-$ ION (G-E RING)

Type of force constants	Symbol for force constant	Atoms involved	Value
Stretching	f_{R1}	Co—O	1.998
	f_{R2}	Co—N	1.342
	f_{R3}	Co—N	1.690
	f_{R4}	Co—O	1.872
	f_{r1}	O—C	7.104
	f_{r2}	C—C	5.749
	f_{r3}	C—N	5.074
	f_{r4}	N—C	5.191
	f_{r5}	C—C	5.332
	f_{r6}	C—N	5.013
	f_{r7}	N—C	5.117
	f_{r8}	C—C	5.429
	f_{r9}	C—O	6.785
	$f_{\alpha 1}$	N$\hat{\text{Co}}$O	1.109
	$f_{\alpha 2}$	N$\hat{\text{Co}}$N	1.094

[a]All stretching force constants are in units of mdynÅ^{-1}, bending in mdynÅ rad^{-1} and stretch-stretch interaction in mdynÅ rad^{-1}.

TABLE-4

FORCE CONSTANTS[a] OF [Co(EDTA)]$^-$ ION (R RING)

Type of force constants	Symbol for force constant	Atoms involved	Value
Stretching	f_{R1}	Co—N	1.099
	f_{R2}	Co—O	1.983
	f_{R3}	Co—N	1.035
	f_{R4}	Co—O	2.012
	f_{r1}	N—C	5.270
	f_{r2}	C—C	5.210
	f_{r3}	C—O	6.425
	f_{r4}	N—C	5.288
	f_{r5}	C—C	5.319
	f_{r6}	C—O	6.319
	$f_{\alpha 1}$	N$\hat{\text{Co}}$O	0.008
	$f_{\alpha 2}$	N$\hat{\text{Co}}$O	0.006
	$f_{\alpha 3}$	N$\hat{\text{Co}}$O	0.008
	$f_{\alpha 4}$	N$\hat{\text{Co}}$O	0.005
	f_{R1r1}	Co—N N—C	0.006
	f_{r1r2}	N—C C—C	0.004
	f_{r2r3}	C—C C—O	0.003

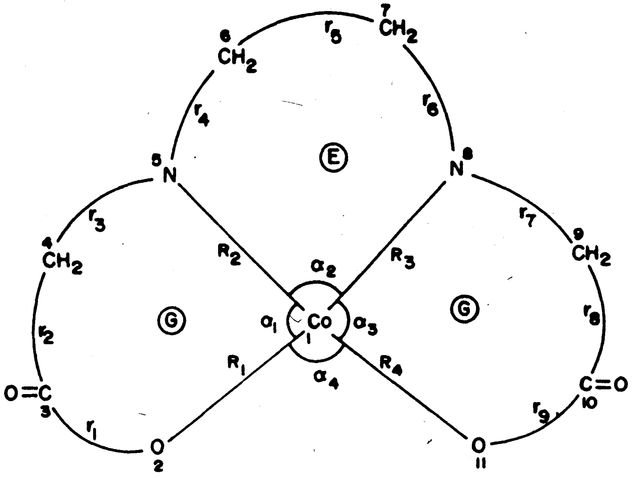

Fig. 6 Internal coordinates for [Co(EDTA)]⁻ ion (G–E ring).

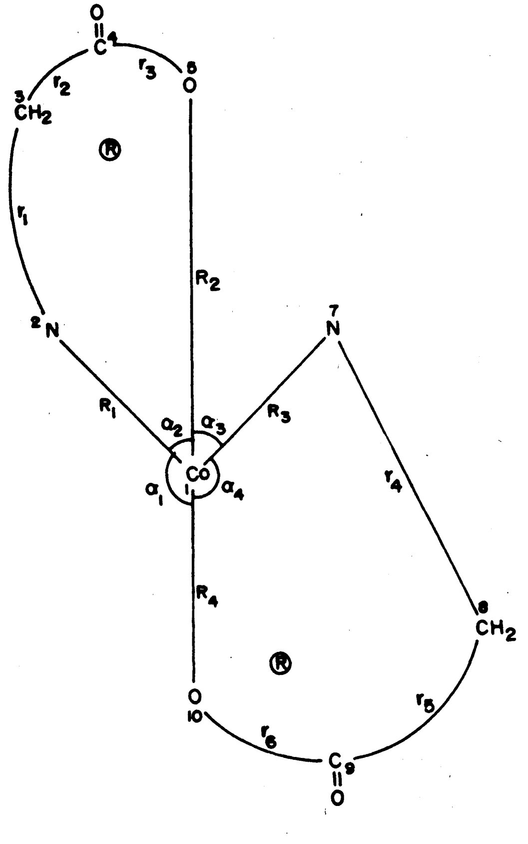

Fig. 7 Internal coordinates for [Co(EDTA)]⁻ ion (R ring).

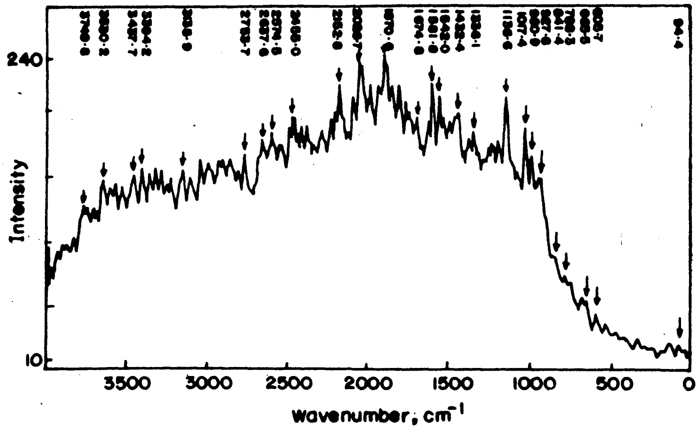

Fig. 8 Raman spectrum of $Na[Co(EDTA)]\cdot 4H_2O$

[a]All stretching force constants are in units of mdynÅ^{-1}, bending in mdynÅ rad^{-1} and stretch-stretch interaction in mdynÅ rad^{-1}.

Nakagawa and Shimanouchi[10] have determined the metal-ligand force constants of metalammine complexes, such as, $[Co(NH_3)_6]^{3+}$ and reported that the stretching force constant of the Co—N bond in $[Co(NH_3)_6]^{3+}$ ion is 1.05 mdynÅ^{-1}. Hiraishi *et al.*[11] and Shimanuchi and Nakagawa[12] have reported nearly the same value for Co—N bond in several similar complexes. This value agrees well with the calculated value of the stretching force constant of the Co—N bond in the R ring of [Co(EDTA)]⁻ ion, determined by the authors in the present investigation. The agreement is poor considering the force constant of the Co—N bond in the G–E rings.

A critical examination of the force constants of Co—N bond in G-E and R rings reveals that the calculated Co—N force constant is larger in the G-E ring than that in the R ring. This may be accounted for by the authors, suggesting that the two nitrogen atoms of ethylenediaminetetraacetate anion are bound tightly through the two methylene groups and the cobalt atom so as to form a strong and stable five-membered E ring and since such a rigid ring structure is absent in the R ring, Co—N bond in the R ring is weaker than that in the G-E ring.

The authors found that the mean stretching force constants of C—O bond of COO⁻ in G–E and R rings are 6.945 and 6.372 mdynÅ^{-1} respectively. As expected, the C—O stretching force constant in G–E ring is found to be higher. In addition, the value of C—O stretching force constant in the present investigation agrees fairly well with that reported by Mohan Murugan.[13] The results indicate that the mean stretching force constants of C—C bond in the environment —O—CO—CH_2— in G–E and R rings are 5.589 and 5.265 mdynÅ^{-1} respectively and that in the E ring in the environment —N—CH_2—CH_2—N— is 5.332 mdynÅ^{-1}. Analysis of these data reveals that the C—C bond is stronger in the G–E rings than in the R rings. This observation is similar to the one already observed by the authors for the force constant of the C—O bond.

A critical examination of the structure of [Co(EDTA)]$^-$ ion has revealed that the C—N bond has two types of environment, *viz.*, —CO—CH$_2$—N— and —N—CH$_2$—CH$_2$—N— in the G-E rings. The mean C—N stretching force constant in the first environment is found to be 5.096 mdynÅ^{-1}, and that in the second environment is 5.101 mdynÅ^{-1}. In the R ring, only the first type of environment is present and the mean C—N stretching force constant is found to be 5.278 mdynÅ^{-1}. Murugan[14] has carried out a normal coordinate treatment on a series of organic compounds and has reported the force constants which agree with the values reported by the authors.

The authors found that the C—N stretching force constants for the three types of C—N bond in [Co(EDTA)]$^-$ ion are 5.096, 5. 278 and 5.102 mdynÅ^{-1} and these values agree fairly well with those reported by Murugan.[14]

A comparative analysis of the values of the stretching force constants of Co—O, Co—N, C—O, C—C and C—N bonds between G—E and R rings (Table 5) reveals that all the stretching force constants in the G—E rings are larger than the respective force constants in the R rings, except for the Co—O and C—N bonds.

The C—N stretching force constant in the R ring is larger than that in the G-E ring. The authors suggest that the electron withdrawing effect towards —CH$_2$ groups, exerted on the two nitrogen atoms of ethylenediaminetetraacetato ligand by the two methylene groups to form the stable E ring, is responsible for the weakening of the C—N bond in the environment —CO—CH$_2$—N—CH$_2$. Since this kind of electron withdrawing effect is absent in the R ring, the authors suggest that this might be the cause for the higher value of the force constant of the C—N bond in the R ring. Since the C—N bond is immediate to the E ring the effect is expected to be appreciable. For the subsequent bonds, the transmission of this effect is reduced considerably due to distance factor and hence the difference between the corresponding bonds in the G-E and R rings is not much, as is evident from the data in the Table 5.

TABLE-5

FORCE CONSTANTS OF SELECTED BONDS IN [Co(EDTA)]$^-$ ION

Nature of bond	Force constant, mdynÅ^{-1}	
	G-E ring	R ring
Co—O	1.935	1.998
Co—N	1.516	1.067
C—O	6.945	6.372
C—C	5.589 (—CO—CH$_2$—N—) 5.332 (—N—CH$_2$—CH$_2$—N—)	5.265
C—N	5.096 (—CO—CH$_2$—N—) 5.102 (—N—CH$_2$—CH$_2$—N—)	5.278

Thus determination of force constants of Co—O, Co—N, C—O, C—C and C—N bonds in Na[Co(EDTA)]·4H$_2$O based on infrared and Raman spectra, confirms its octahedral structure.

ACKNOWLEDGEMENTS

The authors thank the Principal and Head of the Department of Chemistry, Bishop Heber College, Tiruchirapalli for providing facilities and UGC for the award of fellowship to T. Venkatachalam.

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(*Received:* 17 February 1997; *Accepted:* 2 June 1997) AJC-1276