

## Chelates of Nickel (II) with certain polyaminocarboxylic acids

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(Received 3rd June, 1982)

**Summary:** Ten chelates of Nickel (II) with different polyaminocarboxylic acids which were successful in removing nickel from body organs (*in vivo*) and from their sub-cellular fractions (*in vitro*) of experimentally poisoned rats, were prepared and characterised. Their structure has been investigated on the basis of infra red spectral and magnetic moment data. The experimental data suggest that all the complexes are tetra-co-ordinated with  $sp^3$  hybridization having tetrahedral geometry.

### Introduction

Complexes of nickel with polyaminocarboxylic acids such as nitrilotriacetic acid (1), ethylenediaminetetraacetic acid (2-4), diethylenetriamine pentaacetic acid (5), triethylenetetraminehexaacetic acid (6,7) and hexamethylenediaminetetraacetic acid (8) have been studied in solution or in solid state and their structure investigated through infrared spectroscopy (3,4,9,10). Recently, preparation, infrared spectra and thermal stability in solid state of the complexes of nickel with ethylene diaminediacetic acid type ligands have been reported (11). This communication deals with the preparation and characterisation of the complexes of nickel with several polyaminocarboxylic acids, most of which were successful in removing nickel from the body organs (*in vivo*) and from their sub-cellular fractions (*in vitro*) of experimentally poisoned rats probably as chelates (12,13). Their structure has been discussed mainly on the basis of infrared spectral and magnetic moment data.

### Experimental

#### *Reagents*

The following polyaminocarboxylic acids were obtained commercially for this investigation:

1. Ethylenediamine N, N-bis-(O-hydroxyphenyl) acetic acid (EDDHA), Fluka, (Swiss).
2. Ethylenediamine N,N diacetic acid (EDDA), Fluka, (Swiss).
3. N-(2-Hydroxyethyl) ethylenediamine triacetic acid (HEDTA), Aldrich (USA).
4. Nitrilotriacetic acid (NTA), E. Merck (Germany).
5. Ethylenediamine tetraacetic acid (disodium salt, dihydrate) (EDTA), E. Merck (Germany).
6. 1,2 Cyclohexylenediamine tetracetic acid (hydrate), (CDTA) E. Merck (Germany).
7. 3,6 - Dioxoacetamethylenediamine tetraacetic acid (DDTA), E. Merck (Germany).
8. Hexamethylene 1,6 diamino N,N, N'N' tetraacetic acid, (HDTA) Fluka (Swiss).

9. Ethyleneglycol - bis (2-aminoethyl) tetraacetic acid (EGATA), Fluka (Swiss).
10. Diethylenetriamine pentaacetic acid (DTPA), E. Merck (Germany).

#### *Determination of Stoichiometry:*

The composition of the complexes of nickel with various polyaminocarboxylic acids was determined by mole ratio or spectrophotometric titration (14) and Job's method of continuous variation (15).

#### *Preparation of complexes:*

Aqueous solutions of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and a ligand\* were mixed in an appropriate proportion, pH adjusted to 5.6 with 0.1M acetate buffer and stirred for 3 hrs at  $37^\circ$ . The addition of ethanol was necessary to precipitate the complex in all the cases except EDDHA. The complexes were washed with 50% ethanol followed by ether and dried at  $110^\circ$ . They were analysed for nitrogen by the microanalytical technique and for nickel by a standard procedure (16).

#### *Magnetic moment and infrared spectra*

Guoy's method(17) was employed to measure the magnetic susceptibility of the complexes. The infrared spectra of free ligands and their complexes with nickel were recorded on Perkin-Elmer model 577 infrared spectrophotometer in the region  $4000 - 400 \text{ cm}^{-1}$  as KBr. disc.

### **Results and Discussion**

The experimental data on the complexes have been recorded in table 1. All the complexes possess 1:1(M:L) stoichiometry except that of HDTA which has a mole ratio 2:1. All of them decomposed at high temperature

without melting and were insoluble in ethanol, chloroform, dimethylformamide and dioxane. All the complexes except that of EDDHA were soluble in water. The magnetic moment data clearly indicate that all the complexes were paramagnetic to the extent of two unpaired electrons.

Infrared absorptions associated with different modes of vibrations occur in the range  $4000 - 400 \text{ cm}^{-1}$  in the spectra of free ligands and their complexes with nickel but only those of diagnostic value in understanding the structure have been recorded in table 2.

A band of medium intensity at  $3128 - 3000 \text{ cm}^{-1}$  in the spectra of all polyaminocarboxylic acids have been assigned to C-H in  $\text{CH}_2$  groups(3,18,19) which appears as a doublet between  $2960 - 2880 \text{ cm}^{-1}$  in the spectra of the corresponding complexes with nickel indicating the formation of chelate. The characteristic vibration  $\sim 2900 \text{ cm}^{-1}$  for C-H band in chelated molecules further suggests that the  $\text{COO}^-$  groups of the polyaminocarboxylic acids are directly attached to nickel (3). The double peaks for this vibration may be due to some difference between  $\text{CH}_2$  groups, probably the presence of one or more carboxylate groups not bound to the metal (3).

Five absorptions associated with the carboxyl groups are most important since their frequencies have been used in determining the nature of the metal-oxygen linkage viz covalent or ionic and in distinguishing between protonated, co-ordinated and free carboxylic acid( $\text{COOH}$ ) group, (i)  $2850 - 2600 \text{ cm}^{-1}$  ( $\nu\text{OH}$ ) (ii)  $1750 - 1700 \text{ cm}^{-1}$  ( $\nu\text{C=O}$ ) (iii)  $1230 - 1200 \text{ cm}^{-1}$  ( $\text{COOH}$ ) (20-22). The  $\nu\text{OH}$  band is generally of weak intensity and

\* As polyaminocarboxylic acids were insoluble in water, their sodium salts were prepared by adding 10%  $\text{NaHCO}_3$  before reaction with nickel sulphate.

Table 1. Experimental data on the complexes of nickel with some polyaminocarboxylic acids.

Complex	Stoichiometry (Ni:l)	Colour	M.P. (°C)	Analysis found Ni (Calcd.) <sub>N</sub> (%)	Magnetic moment (μ <sub>eff</sub> -B.M.)
1. [Ni.EDDA].3C <sub>2</sub> H <sub>5</sub> OH.H <sub>2</sub> O	1:1	Blue	320-21 d	14.25 (15.10) 7.39 (7.20)	2.98
2. [Ni.(H)EDDHA].2H <sub>2</sub> O	1:1	Grey	250-52 d	12.65 (12.96) 6.45 (6.18)	2.99
3. [Ni.(H)HEDTA].3C <sub>2</sub> H <sub>5</sub> OH.3H <sub>2</sub> O	1:1	Blue	320-21 d	10.00 (11.14) 5.93 (5.31)	3.13
4. [Ni.NTA(H <sup>+</sup> )].5C <sub>2</sub> H <sub>5</sub> OH.4H <sub>2</sub> O	1:1	Green	200-02 d	10.85 (10.67) 2.28 (2.54)	2.38
5. Na[Ni.(H)EDTA].C <sub>2</sub> H <sub>5</sub> OH.3H <sub>2</sub> O	1:1	Blue	205-06 d	12.20 (12.47) 6.14 (5.94)	4.34
6. Na[Ni.(H)CDTA].4C <sub>2</sub> H <sub>5</sub> OH.4H <sub>2</sub> O	1:1	Blue	270-71 d	8.25 (8.62) 3.93 (4.11)	2.86
7. Na <sub>2</sub> [Ni.DDTA].4C <sub>2</sub> H <sub>5</sub> OH.3H <sub>2</sub> O	1:1	Blue	250-52 d	7.50 (8.16) 3.91 (3.89)	4.35
8. [2Ni.HDTA].4C <sub>2</sub> H <sub>5</sub> OH.3H <sub>2</sub> O	2:1	Blue	280-81 d	16.03 (16.79) 3.68 (4.00)	3.43
9. Na <sub>2</sub> [Ni.EGATA].4C <sub>2</sub> H <sub>5</sub> OH.4H <sub>2</sub> O	1:1	Blue	300-02 d	8.13 (7.96) 3.47 (3.80)	3.21
10. Na[Ni(H <sub>2</sub> )DTPA].2H <sub>2</sub> O	1:1	Blue	260-62 d	10.38 (11.56) 8.61 (8.27)	3.75

d = decompose.

thus more limited in usefulness than the other two. The  $\nu\text{C}=\text{O}$  occurs regardless of the manner in which it may be bounded and it is this vibration which gives rise to two regions of absorption not associated with the  $\text{COOH}$  group. The third band is unambiguously associated with the  $\text{COOH}$  group and has been reported to represent  $-\text{CH}_2\text{COOH}$  group in certain metal chelates of EDTA (20). The other two absorptions associated with the carboxyl group are both the manifestations of  $\text{C}=\text{O}$  stretching vibrations, the first being the strongest and most characteristic arising from the co-ordinated carboxyl group occurring at  $1700\text{-}1600\text{ cm}^{-1}$  depending upon the nature of co-ordination linkage (18,20,21). The frequency of the  $\text{C}=\text{O}$  group in some EDTA chelates have been used earlier as an indication of the covalent character for metal-carboxylate bond (18,23-25). An increase in the frequency corresponds to an increase in the covalent character. Thus, when the band occurs at  $1660\text{-}1630\text{ cm}^{-1}$  the bonding is essentially covalent but when it approaches  $1600\text{ cm}^{-1}$ , it is to be considered ionic (3,26). The fifth absorption is associated with the  $\text{C}=\text{O}$  stretching vibration of free ionized carboxyl group which generally occurs at  $1630\text{-}1550\text{ cm}^{-1}$ .

The spectra of all free polyaminocarboxylic acids clearly show three distinct absorptions, a weak band at  $2985\text{ - }2780\text{ cm}^{-1}$ , a strong to very strong and at  $1750\text{ - }1610\text{ cm}^{-1}$  and a medium band at  $1240\text{ - }1215\text{ cm}^{-1}$ . The first two bands are attributed to  $\nu\text{OH}$  and  $\nu\text{C}=\text{O}$  in  $\text{COOH}$  group and the third to  $-\text{CH}_2\text{COOH}$  vibration. In addition, the spectrum of  $\text{Na}_2\text{H}_2\text{EDTA}$  also shows a very strong band at  $1625\text{ cm}^{-1}$  and another at  $1394\text{ cm}^{-1}$  which have been

well recognised as  $\nu\text{C}=\text{O}$  of free ionized carboxylate group (18,27,28). The two bands at  $1660\text{ - }1580\text{ cm}^{-1}$  and at  $1410\text{ - }1390\text{ cm}^{-1}$  in the spectra of other free polyaminocarboxylic acids observed in the present investigation may be assigned to the similar vibrations resulting from  $\text{NH}^+ - \text{CH}_2\text{COO}^-$  grouping as in cases of  $\alpha$  - aminoacids. Since the absence of bands in these regions in the spectra of unco-ordinated NTA and HDTA, the formation of  $\text{NH}^+ - \text{CH}_2\text{COO}$  grouping may not have been possible due to occurrence of close  $\text{COOH}$  groups in the two ligands.

The spectra of corresponding complexes with nickel show two distinct strong absorptions at  $1610\text{-}1580$  and at  $1430\text{-}1395\text{ cm}^{-1}$  which may be recognised as asymmetric and symmetric stretchings of the  $\text{COO-Ni}$  linkage well in agreement with the data on the complexes of different polyaminocarboxylic acids with nickel and other metals (11,26,29). Further the appearance of asymmetric stretching or the main vibration of  $\text{C}=\text{O}$  groups  $\sim 1600\text{ cm}^{-1}$  strongly suggests the ionic character of  $\text{COO-Ni}$  bond in our complexes. The difference between asymmetric and symmetric stretching vibrations of co-ordinate carboxyl group indicates the degree of covalent bonding in  $\text{COO} - \text{metal}$  grouping. The frequency difference increases as bonding becomes more covalent. Thus, if the difference is generally  $225\text{ cm}^{-1}$  or greater the bonding is considered to be primarily covalent and if it is less than  $225\text{ cm}^{-1}$ , the bonding is primarily ionic (11,26,29). Since the difference between asymmetric and symmetric stretching vibrations of  $\text{COO-Ni}$  grouping in the present work, range

from  $173-223\text{ cm}^{-1}$ , the bonding between nickel and carboxyl group appears to be essentially ionic in these complexes. The spectra of the complexes of NTA and HDTA with nickel show splitting of the strong asymmetric stretching of COO-Ni bonding at  $1600\text{ cm}^{-1}$  which is probably due to a crystalline state effect as observed by the other workers (29,30). In case of Ni-NTA complex, this split band at  $1610$  and  $1580\text{ cm}^{-1}$  may be assigned to a non-bonding co-ordinate carboxyl group(29) and the strong absorption at  $1660$  may represent the occurrence of  $\text{NH}^+ - \text{CH}_2\text{COO}^-$  in the molecule (31). In addition to the asymmetric stretching vibration of the co-ordinate carboxyl group, the spectra of some of the nickel complexes show a prominent shoulder at  $1560\text{ cm}^{-1}$  which appears to be due to presence of free ionised  $\text{COO}^-$  group in these complexes (18,19). The lower band of this vibration at  $\sim 1400\text{ cm}^{-1}$  could not be identified as it is probably masked by the strong vsymm. COO-Ni vibration at almost same position.

Another absorption of diagnostic significance is due to the C-N bond which has been observed at  $1130-1080\text{ cm}^{-1}$  in the spectra of different metal chelates of EDTA(3,20,26). The frequency of this vibration increases as the metal-N bond becomes more covalent(3). The medium band at  $1205-1132\text{ cm}^{-1}$  in the spectra of free polyaminocarboxylic acids may be assigned to the C-N bond. This absorption undergoes a considerable negative shift on complexation due to the electron drainage from the N atom of the ligands(32). The band loca-

ted at  $1124-1096\text{ cm}^{-1}$  in the spectra of the corresponding complexes of nickel may thus be due to the C-N bond. Such a shift offers strong evidence for the co-ordination of N atoms of these ligands to the Ni ion(21). Another weak absorption appearing at a slightly higher frequency at  $1320-1258\text{ cm}^{-1}$  in the spectra of all the chelating agents and in those of their corresponding complexes with nickel in the present study may also be assigned to the C-N bond. This might have been due to  $\text{COO}^-$  group but as an absorption has frequently been observed in this range in the spectra of ethylene-diamine and other similar amines, the band has been preferred to be due to C-N(3,26). However, this absorption seems to be insensitive to the co-ordination. The spectra of the complexes also show peaks at  $3580-3420\text{ cm}^{-1}$  and at  $3420-3220\text{ cm}^{-1}$  which could easily be assigned to  $\nu\text{OH}$ , in free  $\text{H}_2\text{O}$ (18,22,33) and in  $\text{C}_2\text{H}_5\text{OH}$ (32,34) respectively, owing to the presence of these as the molecule of crystallization in the complexes.

Almost all the complexes examined are blue and are paramagnetic having, u.eff. ranging from 2.38 to 4.35 B.M. which is characteristic of tetrahedral structure(35). The higher value of magnetic moment than expected for a  $d^8$  system in tetrahedral field having two unpaired electrons is due to the high orbital contribution to the magnetic moment. Such complexes are reported to have a value in the range 3.5 to 4.2 B.M., which is fairly close to the present observation. It is, therefore, obvious that the complexes are tetra co-ordinated with  $sp^3$  hybridization

Table 2. Relevant infrared absorption frequencies ( $\text{cm}^{-1}$ ) of polyaminocarboxylic acids and their complexes with Nickel.

	$\nu\text{C-H}(\text{CH}_2)$	$\nu\text{OH}$ (COOH)	$\nu\text{C=O}$ (COOH)	$\nu\text{COO-}$ (free)	$\nu\text{Asym.}$ (COO-Ni)	$\nu\text{COO-}$ (free)	$\nu\text{Symm.}$ (COO-Ni)	$\nu\text{COOH}$ ( $\text{CH}_2\text{COO-}$ H)	$\nu\text{C-N}$	$\Delta\nu\text{Asymm.}$ $\text{Symm.}$ (COO-Ni)
1. ( $\text{H}_2$ )EDDA	3058m(br)	2828m	1613vs	1580vs		1394s		1230m	1320s 1185w	
1a. [Ni.EDDA]. $3\text{C}_2\text{H}_5\text{OH}$	2950m									
$\text{H}_2\text{O}$	2927m				1583vs		1395s		1305s 1122w 188	
2. ( $\text{H}_2$ )EDDHA	3092m(br)	2920w	1640vs	1600s		1410w		1226sh	1275m 1177w	
2.a [Ni.(H)EDDHA]. $2\text{H}_2\text{O}$	2930w 2880w	2730w 2600w	1655sh 1642vs		1605vs		1432s	1226m	1273m 1096m 173	
3. ( $\text{H}_3$ )HEDTA	3020m 3000m	2984w 2944w	1685m	1625vs		1390s		1215w	1300w 1197w	
3a. [Ni.(H)HEDTA]	2980sh	2860w	1730m		1610vs		1400s	1225w	1316w 1100m 210	
$3\text{C}_2\text{H}_5\text{OH}.3\text{H}_2\text{O}$	2934w									
4. ( $\text{H}_3$ )NTA	3035m	2985w	1730s					1223w	1332w 1205m	
4a. [Ni.NTA( $\text{H}^+$ )]				1660s	1610sh		1396m		1320m 1118s 199	
$5\text{C}_2\text{H}_5\text{OH}.4\text{H}_2\text{O}$	2927w			(NH $\pm$ CH $_2$ COO-1)	1580vs					
5. $\text{Na}_2(\text{H}_2)\text{EDTA}.2\text{H}_2\text{O}$	3030s	2780w	1670vs	1625vs (br)		1394vs (br)		1223w	1290m 1192m	
5a. $\text{Na}[\text{Ni}(\text{H})\text{EDTA}].\text{C}_2\text{H}_5\text{OH}.3\text{H}_2\text{O}$	2955w 2930w	Masked by noise.	1717m	1572sh	1603vs	1435w	1395m-s	1222m	1300w 1108w 208	
6. ( $\text{H}_4$ )CDTA	3000m 2955w	2865w	1748vs 1727s 1704s	1652m 1585s		1400s		1233m	1265m 1168m	
6a. $\text{Na}[\text{Ni}(\text{H})\text{CDTA}].4\text{C}_2\text{H}_5\text{OH}.4\text{H}_2\text{O}$	2935m	2860w	1660sh	1560sh	1595vs		1392s	1230w	1258m 1110s 203	
7. ( $\text{H}_4$ )DDTA	3052m	2868w	1740s	1635m				1225w	1278w 1132m	
7a. $\text{Na}_2[\text{Ni}(\text{H})\text{DDTA}].4\text{C}_2\text{H}_5\text{OH}.3\text{H}_2\text{O}$	2920w 2880sh			1560s (sh)	1600vs		1400s		1300sh 1100sh 200	
8. ( $\text{H}_4$ )HDTA	3128m 3015m	2868w	1718s 1684s					1215w	1307w 1170w	
8a. [2Ni.HDTA]. $4\text{C}_2\text{H}_5\text{OH}.3\text{H}_2\text{O}$	2960m 2930m				1638sh 1608vs		1400s		1300w 1105s 223	
9. ( $\text{H}_4$ )EGATA	3055m	2869w	1737s (br) 1720sh	1637m (br)		1400m		1225w	1280w 1134m	
9a. $\text{Na}_2[\text{Ni}(\text{H})\text{EGATA}].4\text{C}_2\text{H}_5\text{OH}.4\text{H}_2\text{O}$	2964w 2920m			1560sh	1600vs(br)		1400s		1300w 1124m 200	
10. ( $\text{H}_5$ )DTPA	3065m 3010m	2850w	1730vs 1695vs	1632vs		1395s		1240m	1295w 1200m 1176w	
10a. $\text{Na}[\text{Ni}(\text{H}_2)\text{DTPA}].2\text{H}_2\text{O}$	2965w 2925w		1727m(br)	1560sh	1600vs(br)		1400s	1220w(br)	1100m 200	

w = weak, m = medium, s = strong, v = very, br = broad, sh = shoulder

having tetrahedral geometry. The ethanol and water molecules in the solid state are obviously outside the co-ordination sphere.

### Acknowledgement

The authors are grateful to Director, Central Drug Research Institute, for the estimation of nitrogen and recording infra red spectra of the complexes.

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