The Properties and Infrared Absorption Spectra of Nitrilotriacetate Chelates[*]

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The metal chelate-forming behavior of nitrilotriacetic acid (hereafter referred to as NTA) has been studied in terms of their properties in a solution,[1] but very few investigations have been undertaken into the NTA chelates in a solid state.[2] Extensive investigation into ethylenedinitrilotetraacetic acid (hereafter referred to as EDTA) chelates, both in a solution and in solid states have proved that the bonding between the EDTA and divalent metals is primarily ionic.[3] In those investigations, infrared absorption spectroscopy provided much information on the nature of the bonding between metal and ligand. For instance, the absorption band for the carbonyl bond of the carboxylate groups was found to shift to higher frequencies with the increasingly covalent character of the metal-carboxylate bond. This observation made it possible to determine whether the bonding in EDTA chelates is essentially ionic or covalent. At the same time, the infrared technique was utilized in differentiating coordinated and uncoordinated carboxyl groups.[4,5] However, this differentiating technique is not always successful; in those complexes whose bonding is primarily ionic, the absorptions of the COOM group and those of the uncoordinated COO^- group occur in the same region, so it is not possible to distinguish between these two cases.

This study, concerned with some of the properties and the infrared spectra of NTA and metal-NTA chelates, attempts to investigate the chelating behavior of NTA in a solid state as well as in a solution and to find a relationship between the carbonyl band and the nature of the metal-carboxylate bond.

Experimental

Infrared Spectra.—The infrared spectra of crystalline complexes were studied in mineral oil mulls and in potassium bromide disks. The solid complexes were pressed into disks, using 0.3∼0.5 mg. of chelate mixed with 100 mg. of potassium bromide for each disk. The infrared spectra in aqueous solutions were also taken for those complexes which are soluble enough in water. The aqueous solutions were made with 99.5% D_2O at concentrations of approximately 3∼15% by weight, and the spectra were observed using a cell with calcium fluoride windows. The measurements were made with a Nippon Koken model DS 301 double-beam spectrophotometer equipped with sodium chloride optics.

Reagents.—The inorganic salts used in preparing the complexes were reagent grade in all cases. The free acid of NTA (donated by Dojindo & Co.) was analytical grade and was used without further purification.

Preparation of NTA Chelates. Sodium Salt of NTA Chelates ($NaM^{II}Y$[6]).—The following metal carbonates were used in preparing solid chelates: $(MgCO_3)_4\cdot Mg(OH)_2\cdot 5H_2O$, $CaCO_3$, $SrCO_3$, $BaCO_3$, $CoCO_3\cdot 3Co(OH)_2$, $NiCO_3\cdot 2Ni(OH)_2\cdot 4H_2O$, $CuCO_3\cdot Cu(OH)_2\cdot H_2O$, $(PbCO_3)_2\cdot Pb(OH)_2$, $ZnCO_3$ and $CdCO_3$. The theoretical amount of inorganic salt was added to a warm suspension of 0.02 mol. of NTA in 50 ml. of water. After complete dissolution, the pH value of the solution was adjusted to 6∼7 by adding a 0.01 M solution of sodium carbonate. The solution was heated almost to boiling. To this solution, 200∼300 ml. of absolute ethanol was added until the precipitates began to appear, and the resulting solution was cooled in an ice-bath. After filtering the crystals, they were recrystallized from a small amount of water. The finished chelates were immediately placed in a vacuum desiccator for 24 hr.

Hydrogen NTA Chelates ($HM^{II}Y$).—These were prepared in a similar manner, but sodium carbonate was not added to the solution. The separated hydrogen NTA chelates were recrystallized from water and placed in a vacuum desiccator for 24 hr.

Analyses.—The chelates were analyzed for alkaline earths and divalent metals by the EDTA titration technique after the samples had been decomposed with concentrated nitric acid and hydrogen peroxide.[7] For the sodium salt of chelates, sodium was determined by precipitating it as sodium-zinc-uranyl-acetate from the decomposed solution,

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[*] Contribution No. 41 from the Department of Organic Syntheses.

[1] G. Schwarzenbach, E. Kampisch and R. Steiner, *Helv. Chim. Acta*, **28**, 828 (1945).

[2] M. Mori, M. Shibata, E. Kyuno and Y. Okubo, This Bulletin, **31**, 940 (1958).

[3] D. T. Sawyer and P. J. Paulsen, *J. Am. Chem. Soc.*, **81**, 816 (1959).

[4] D. H. Busch and J. C. Bailar, ibid., **75**, 4574 (1953).

[5] M. L. Morris and D. H. Busch, ibid., **78**, 5178 (1956).

[6] Y designate the NTA anion dissociated to trivalent state.

[7] Y. Tsuchitani, Y. Tomita and K. Ueno, *Talanta*, **9**, 1023 (1962).

TABLE I. COMPOSITION OF NTA CHELATES INVESTIGATED

Chelate	Metal, %		Sodium, %	
	Calcd.	Found	Calcd.	Found
$NaMgY\cdot 3.5H_2O$	8.16	8.10	7.72	7.68
$NaCaY\cdot 3H_2O$	14.0	14.0	8.05	7.88
$NaSrY\cdot 4H_2O$	23.5	24.0	6.22	6.12
$NaBaY\cdot 3.5H_2O$	33.4	34.0	5.59	5.50
$NaCoY\cdot 2.5H_2O$	18.7	19.0	7.27	7.05
$NaNiY\cdot 3.5H_2O$	17.6	17.0	6.91	6.68
$NaCuY\cdot 2.5H_2O$	19.9	20.6	7.22	7.06
$NaZnY\cdot 3.5H_2O$	19.3	19.4	6.67	6.60
$NaCdY\cdot 3H_2O$	30.3	31.0	6.15	6.08
$NaPbY\cdot 3H_2O$	43.9	44.2	4.87	4.80
$MgHY\cdot 3H_2O$	9.33	9.30		
$CaHY\cdot 2H_2O$	15.1	14.9		
$SrHY\cdot 4H_2O$	25.5	25.4		
$BaHY\cdot 3H_2O$	36.2	36.5		

$Y=N(CH_2COO)_3^{3-}$

followed by EDTA titration.[8,9] The results of the analyses are shown in Table I, along with the proposed formulae.

Results and Discussion

Spectra of Ligand.—In Table II, assignments and wave numbers are given for the important peaks of the NTA chelates of the alkaline earth metals (Mg, Ca, Sr, Ba), divalent metals (Cu, Ni, Zn, Co, Pb) and sodium salts of NTA. There is no significant absorption band between 4000 and 1800 cm^{-1} except for the bands in the 3000~2800 cm^{-1} region, which are assigned to the C–H streching vibration of the CH_2 groups.

The carboxyl group is known to give a strong band in the range between 1735 and 1550 cm^{-1} which is due to the C=O stretching vibration.[10] As it is believed, from the acid dissociation constant data, that NTA ligand acid has a zwitter ion structure, as in the case of EDTA, one may expect a band for carboxylate ion in the 1610~1550 cm^{-1} region for the acid form of NTA. However, no significant absorption band could be found in this region for the free ligand acid. Therefore, it is doubtful that NTA has a zwitter ion structure in the solid state. This situation will be made clearer if one could compare the spectra of the solid state with that of the solution state. However, the spectra of the aqueous solution could not be measured because of the poor solubility of the ligand acid. In this connection, it is noteworthy that a similar situation has been reported for EDTA ligand acid, where no clear band of carboxylate ions, could be found in the expected region. Therefore, the existence of a zwitter ion structure was thought to be doubtful[11] in the solid state, although a very weak shoulder at

TABLE II. INFRARED ABSORPTION PEAKS FOR NTA CHELATES OF ALKALINE EARTH METALS AND DIVALENT METALS

	Stability constant	Ionic radius	-COOH	-COOM	Hydrated -COO$^-$	Crystal -COO$^-$	-CN	D_2O solution -COOM
H_3Y			1728					
Na_2HY			1673		1638	1399		1625
Na_3Y	2.1				1580	1411	1138	1588
$NaMgY\cdot 3.5H_2O$	5.41	0.98		1623	1588	1410	1135	
$MgHY\cdot 3H_2O$			1660	1625				
$NaCaY\cdot 3H_2O$	6.41	1.01		1640	1600	1428	1131	
$CaHY\cdot 2H_2O$			1705	1645				
$NaSrY\cdot 4H_2O$	4.98	1.18		1612	1588	1416	1131	
$SrHY\cdot 4H_2O$			1680	1616				
$NaBaY\cdot 3.5H_2O$	4.82	1.34		1608	1588	1416	1131	
$BaHY\cdot 3H_2O$			1680	1613				
$NaCoY\cdot 2.5H_2O$	10.38	0.78		1622		1411	1127	1596
$NaNiY\cdot 3.5H_2O$	11.53	0.67		1621		1415	1123	1594
$NaCuY\cdot 2.5H_2O$	12.96	0.69		1635* 1667 1604		1418	1115	1612
$NaZnY\cdot 3.5H_2O$	10.67	0.70		1624		1412	1127	1599
$NaCdY\cdot 3H_2O$	9.83	0.92		1619		1416	1129	
$NaPbY\cdot 3H_2O$	11.39	1.17		1625		1414	1123	1599

* Anhydrated solid

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[8] H. Flaschka, *Mikrochemie ver. Mikrochim. Acta*, **39**, 315 (1952).

[9] B. Sen, *Z. anal. Chem.*, **157**, 2 (1957).

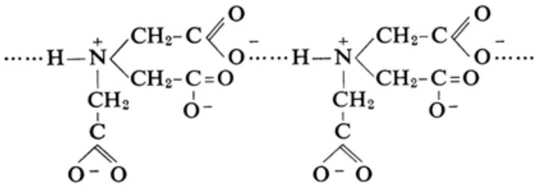
[10] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y. (1958), p. 162.

[11] D. Chapman, *J. Chem. Soc.*, **1955**, 1766.

	H_3Y	H_2Y^-	HY^{2-}	Y^{3-}
In solution		1720 cm^{-1} 1623 cm^{-1}	1625 cm^{-1}	1584 cm^{-1}
Solid	1728 cm^{-1}		1678 cm^{-1} 1638 cm^{-1}	1580 cm^{-1}

1635 cm^{-1} has been assigned to carboxylate ions by one investigator.[12)]

In contrast to the NTA free acid, its disodium and trisodium salts were easily soluble in water, so that their spectra were observed both in solid and in solution states. The two bands at 1678 cm^{-1} and 1638 cm^{-1} of disodium NTA in a solid state have been assigned to the $-COOH$ and $-COO^-$ groups respectively. However, in an aqueous solution, only one band, at 1625 cm^{-1}, is observed, indicating that all three carboxyl groups exist as $-COO^-$ and that the proton is attached to the nitrogen atom. This situation has been pointed out by Nakamoto, Morimoto and Martell.[13)] Why this singlet carboxyl band splits into a doublet when one goes from a solution to a solid state can be explained in two ways. In one explanation, one of the carboxylate ions of NTA is bonded to the proton of neighboring NTA molecules in the solid state, as is schematically shown below (I). This intermolecular hydrogen bonding will not occur in a solution. The hydrogen-bonded carboxylate group gives rise to an absorption at 1678 cm^{-1}, whereas the free carboxylate group absorps at 1638 cm^{-1}. In another explanation, the stretching vibration of the carboxylate carbonyl bonding will be influenced by the crystal field in the solid state, which will result in the splitting of the singlet band.



I

Trisodium NTA gives only one band, near 1580 cm^{-1}, both in a solid and in a solution, so it is clear that the three carboxyl groups exist as $-COO^-$, regardless of the state.

The shift of the band for the free carboxylate group from 1625 cm^{-1} in disodium salt to 1584 cm^{-1} in trisodium salt may be caused by the loss of a formal positive charge on the nitrogen atom, as has been discussed by Nakamoto.[13)]

The Spectra of Metal Chelates.—It one assumes that NTA behaves as a tetradentate ligand, with all the carboxylate groups coordinated to the central metal ion, only one carboxyl band may be expected in this region for all metal-NTA chelates. However, the infrared spectra of NTA chelates of alkaline earth metals in a solid state show two carboxyl bands, as Table II indicates.

The first group of bands appears in the range between 1640 and 1600 cm^{-1} and can be found in the alkaline earth chelates but in neither free ligand acid nor sodium salts. Therefore, this band can be assigned to the coordinated carboxylate groups. The second group of bands appears in the range between 1600 and 1580 cm^{-1} and can be found in the trisodium salt of NTA as well as in the alkaline earth chelates. However, in the case of the hydrogen complexes and the free acid of NTA, this band has completely disappeared and a new band has appeared around 1700 cm^{-1}, where the absorption band of free carboxylic acid is expected. Therefore, it is quite probable that the band at 1600∼1580 cm^{-1} is associated with the uncoordinated carboxylate ions. Similar spectral characteristics have been observed in EDTA chelates, where the coordinated carboxylate group, the uncoordinated carboxyl group and free carboxylic acid were assigned to the bands near 1650, 1750 and 1600 cm^{-1} respectively. From these observations, it is probable that, in the alkaline earth chelates, one of the three carboxyl groups does not coordinate with the central metal ion, but remains free carboxylic acid or carboxylate ions. This conclusion may not be extended to the chelating behavior of NTA in a solution, however, since the spectra were taken on solid samples only and no information on the spectra of the solution state could be obtained because of their poor solubility.

In the case of divalent metal ions other than alkaline earth metals, their chelates

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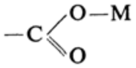
12) D. T. Sawyer and P. J. Paslsen, *J. Am. Chem. Soc.*, **80**, 1597 (1958).

13) K. Nakamoto, Y. Morimoto and A. E. Martell, ibid., **84**, 2081 (1962).

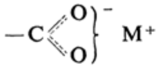
showed a single band, with a shoulder in the carbonyl region. This suggests that NTA behaves as a tetradentate ligand, with all carboxylate groups coordinated with the central metal ion. This is also supported by the information obtained from the spectra of an aqueous solution, in which the shoulder of the carboxyl band disappears and the carboxyl band does not change when the hydrogen complex (HMY) is converted into a sodium complex (NaMY).

Regarding EDTA metal chelates, many papers have been published on the relationship between the carbonyl frequency of a coordinated carboxylate group and the covalent character of the metal-carboxylate bond. Sawyer and Paulsen³⁾ have summarized the previous data on the EDTA chelates and have concluded as follows: When the coordinated carboxylate band ($\nu_{C=O}$) appears in the 1610~1550 cm^{-1} region, the bonding is primarily ionic. When this band is in the 1650~1625 cm^{-1} region, the bonding is primarily covalent. When the band occurs between these two region, the bonding is probably partially ionic and partially covalent.

In the case of the NTA chelates investigated, the carbonyl bands are always found to occur in the same region, 1640~1600 cm^{-1}, where the carbonyl band of a so-called primarily or partially covalent character is expected to appear. The carbonyl frequencies, therefore, may not be related to the covalent character of the metal-carboxylate bond, and the general rule for judging the nature of the bonding in EDTA chelates cannot be applied to NTA chelates. However, in the case of alkaline earth chelates, the frequency of the carbonyl band in a solid state decreases in the order of calcium > magnesium > strontium > barium. Interestingly, this order is identical with the decreasing order of the chelate stability constant. The plots of the logarithms of stability constants against the wave numbers of the carbonyl bands show a straight line, as Fig. 1 shows. This parallel relationship in alkaline earth chelates can qualitatively be explained as follows. The increase in the stability of the NTA chelates is related to the increase in the covalent nature of the metal-ligand bond. Although the nature of this bonding is primarily ionic, the degree of the contribution of the covalent form II will be greater than that of the ionic form III; this effect results in an increase in the double-bond character of the carbonyl bond.



II



III

As to the other divalent metal chelates, it is found that the frequency of the absorption band increases with the increasing stability constant, with the exception of nickel chelates. This relationship was observed in both the solid state and in an aqueous solution.

As has been stated previously, the frequency of the carboxylate band of NTA shifted from 1585 cm^{-1} to 1625 cm^{-1} when the nitrogen atom coordinated with a proton. This is understood to be due to the influence of the formal positive charge on the nitrogen atom. For the NTA chelates, in which the coordination of nitrogen atom with the central metal ion is strong, a similar influence on the carboxylate frequency may be expected. For the alkaline earth chelates, the *N*-metal bonding

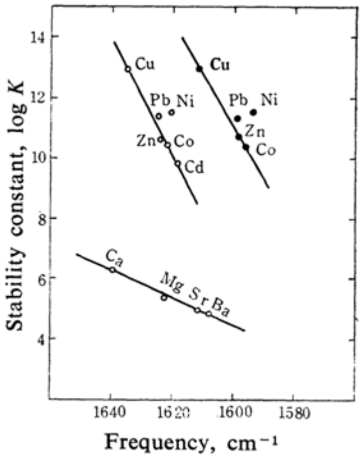


Fig. 1. Correlation of chelate stability constants with C=O absorption frequencies of the chelates.
-○- Hydrated crystal
-●- D_2O solution

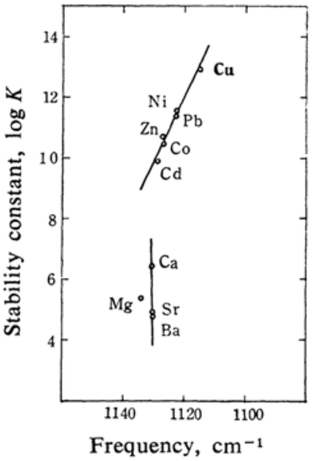


Fig. 2. Correlation of chelate stability constants with C-N absorption frequencies of the chelates.

may not be strong enough to influence the carboxylate frequency. In such a case, the carbonyl frequency must be discussed in relation with the chelate stability.

However, for the NTA chelates of other divalent metals which form more or less strong *N*-metal bonding, their carboxylate frequency will be influenced not only by the carbonyl-metal bonding, but also by the *N*-metal bonding. The coordination of nitrogen atoms to such metal ions is also supported by the shift of the C–N bond, as will be discussed later. Therefore, in this case, one must be careful not to correlate the carboxylate frequency with simply the chelate stability or the nature of the carbonyl-metal bonding.

Carboxylate ions are known to give rise to another peak in the 1420~1390 cm^{-1} region. Accordingly, the band at 1420~1390 cm^{-1} has been assigned to this group, as in Table II. The peak at 1420~1390 cm^{-1} shows some splitting, but no significant relationship between the frequencies of the peaks and the kind of metal ions can be found.

The absorption band in the 1410~1110 cm^{-1} region has been assigned to the C–N bond in NTA chelates.10) The relationship between the chelate stability and the frequency of the C–N bond for NTA chelates is shown in Fig. 2. The alkaline earth chelates give rise to the peak in the same region, at 1130 cm^{-1}, with the exception of magnesium. On the other hand, the C–N bond of the other divalent metal chelates appears in the 1130~1110 cm^{-1} region, and their frequencies decrease with an increasing stability constant. The corresponding band of the trisodium salt of NTA is found at 1138 cm^{-1}. If one assumes that the coordination of nitrogen to the metal ion results in the lowering of the stretching frequency of the C–N bond, these observations indicate that the *N*-metal bond of alkaline earth chelates is relatively weak and is not sensitive to the metal ions, whereas the bond of other divalent metal chelates is relatively strong and is sensitive to the metal ions. This conclusion may be supported by the fact that these divalent metals form a relatively stable ammine complex, while alkaline earth metals do not form a stable ammine complex.

Summary

Infrared absorption spectra have been observed in NTA and its metal chelates, in solid states as well as in solution. The results indicate that NTA does not exist as zwitter ions in the solid state, that it behaves as a quadridentate ligand for such divalent metals as copper, nickel, cobalt, zinc, cadmium and lead, but that it behaves as a terdentate ligand for the alkaline earth metals. It is also found that the wave number of the $\nu_{C=O}$ band of the coordinated carboxylate group in the NTA chelates tends to shift to a higher value with an increasing chelate stability constant.

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