ATRANES

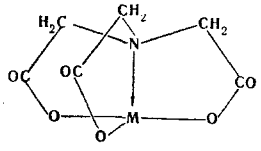
XXIX.* IR ABSORPTION SPECTRA AND STRUCTURES OF METALLOATRANE-3,7,10-TRIONES

M. G. Voronkov, S. V. Mikhailova,
L. A. Ritevskaya, and Ya. A. Éidus

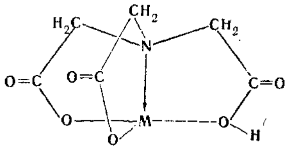
UDC 547.898'25 : 541.49 : 543.422.4

The IR spectra (at 400-2000 cm^{-1}) of chelate metal salts and mixed inorganic anhydrides of aminotriacetic acid (metalloatrane-3,7,10-triones) $N(CH_2COO)_3M \cdot nH_2O$ (M = B, Al, Ga, In, Tl, La, Ce^{III}, Nd^{III}, HOPb^{IV}, ClZr^{IV}, Bi^{III}, Cr^{III}, HOOMo^{VI}, HOOU^{VI}, Fe^{III}, Co^{III}, and Ni^{III}) and, for comparison, of compounds of the $N(CH_2COOM^1)_3$ series (M^1 = H, Li, Na, K) were studied. The degree of ionic character and the character of the metal atom bond with the carboxyl groups was estimated on the basis of the high sensitivity of ν_s and ν_{as} (COO$^-$), which are found at 1360-1450 and 1550-1630 cm^{-1}, respectively, to structural changes in the molecules and from the presence of $\nu_{C=O}$ at 1710-1765 cm^{-1}. The COO$^-$ bonds in compounds with M = Ce^{III}, Nd^{III}, ClZr^{IV}, HOOMo^{VI}, and Ni^{III} are nonequivalent, which compels one to assign structure II with one free carboxyl group to them. The remaining investigated substances have the metalloatrane-3,7,10-trione structure, in which the degree of ionic character of the three equivalent M−O bonds varies over wide limits. The position of the ν_{C-N} absorption band at 1100-1130 cm^{-1} makes it possible to conclude that compounds with M = Fe, Co, Ni, Cr, Bi, ClZr, and HOPb contain the strongest M ← N bond. The absorption maxima at 450-540, 540-560, and 570-640 cm^{-1} are presumably related to both the vibrations of the M ← N bond and to the vibrations of the M−O bonds.

In previous communications [2-4] we described the synthesis of a number of chelate metal salts and mixed inorganic anhydrides of aminotriacetic acid of the $N(CH_2COO)_3M \cdot nH_2O$ type (M is a trivalent metal atom or a trivalent inorganic group of atoms), which are formally (in analogy with metalloatranes [5-8]) called metalloatrane-3,7,10-triones (I).



I



II

The present spectroscopic investigation was undertaken to study the structure of the metalloatrane-3,7,10-triones as well as the nature of the bonds formed in them by the metal atom (ion) with the carboxyl groups and with the nitrogen atom. Some metal salts of aminotriacetic acid have already been investigated by IR spectroscopy [9-21]. However, individual compounds of the I type have been spectroscopically studied only in the case of representatives with M = Al, Sc, Y, and Ln (Ln is lanthanide) [13-15].

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*See [1] for communication XXVIII.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. P. Stuchki Latvian State University, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 753-759, June, 1972. Original article submitted June 18, 1971.

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TABLE 1. Frequencies ($\nu_{as}C=O$, ν_{COO^-}, and ν_{C-N}) of Stretching Vibrations in the IR Spectra of $\overrightarrow{N(CH_2COO)_3M} \cdot nH_2O$*

M	n	$\nu_{as}C=O$, cm^{-1}	$\nu_{as}COO^-$, cm^{-1}	ν_sCOO^-, cm^{-1}	$\Delta\nu$, cm^{-1}	$\nu C-N$, cm^{-1}	Other frequencies, cm^{-1}
H_3	0	1728 vs	—	—	—	1070 m	1459 m, 1434 s, 1411 m, 1383 m 1371 s, 1334 s, 1264 s, 1204 s, 1074, 966 s, 932 w, 900 s, 863 m, 744 s, 671 m, 591 s, 551 m, 483 m
Na_3	0	—	1578 vs	1407 s	172	1140 m	2881 s, 2916 s, 1460 w, 1451 m 1330 s, 1284 s, 1261 m, 984 m, 917 s, 728 m, 506 s, 520 m, 534 s, 583 vs
K_3	0	—	1590 vs	1403 vs	187	1144 m 1133 m	3079 m, 3191 s, 1458 s, 1376 vs 1320 m, 1259 s, 1206 w, 1173 m, 1044 m, 973 s, 964 s, 903 vs, 729 m, 695 s
B	0	1760 vs	—	—	—	1125 m	1490 w, 1475 m, 1460 w, 1378 s, 1267 s, 1267 s, 1167 m, 1034 m, 937 m, 905 s, 770 s, 625 m, 556 m, 425 m
Al	3		1654, 1625	1399	226	1103, 1119	
Al	2		1600 vs	1400 s	200	1130	1236 m, 1206 m, 1010 w, 924 m, 819 m, 632 m, 545 m, 416 m
Al	0		1578	1436	142	1101, 1118	
Ga	2		1576 vs	1394 s	182	1114	1320 m, 1272 m, 1013 m, 912 s, 750 m, 623 s, 564 w, 528 s, 517 s, 428 s
In	2		1588 vs	1384 s	204	1116	908 m, 724 m, 619 m, 545 w, 417 vs
Tl	2		1586 vs	1380 s	206	1116	1333 s, 1230 w, 1024 w, 900 w, 524 s, 416 m
Sc	2		1576	1415	161	1116	
Sc	0		1587	1420	167	1120	
Y[13]	4		1579	1424, 1411	168	1115	
Y[13]	0		1595, 1579	1414, 1401		1120	
La	5		1576, 1560				
La	3		1570 vs	1450 m 1410 m	160	1122	1335 m, 1306 m, 1242 w, 905 m, 912 s, 722 s, 562 m, 499 m, 413 m
La[13]	0		1580	1406	174	1119	
Ce^{III}	3	1720 s	1574 s	1430 s 1400 s	174	1120	1325 m, 1236 s, 1200 s, 1009 m, 966 m, 902 m, 866 w, 744 s, 580 w, 541 m, 482 s
Pr^{III} [13]	5		1577	1420, 1409		1124	
Pr^{III} [13]	3		1578, 1560	1433, 1409		1122	
Pr^{III} [13]	0		1604, 1576	1406		1120	
Nd^{III} [13]	5		1580	1420, 1409		1124	
Nd^{III} [13]	3		1578, 1569	1434		1117	
Nd^{III} [13]	1		1605, 1577	1407		1128	
Nd^{III} [13]	0		1577	1401		1116	
Sm^{III} [13]	4		1588, 1561	1401		1116	
Sm^{III} [13]	3		1579, 1560	1406		1115	
$ClZr^{IV}$	3	1740 s	1610 s	1400 s	210	1074, 1100	1224 s, 1196 s, 964 m, 888 m, 652 s, 604 w, 543 w, 483 m,
$HOPb^{IV}$	2		1570 vs	1390 s	160	1107	900 s, 529 s, 412 m
Bi^{III}	3		1576 vs 1554 s	1389 s	187	1110	1333 s, 1235 m, 1012 w, 902 s, 790 s, 774 m, 726 m, 615 s, 559 m, 507 m
Cr^{III}	3		1590 s	1380 vs	210	1103	1310 m, 1020 m, 1010 m, 985 m, 940 s, 750 s, 620 s, 550 w
$HOOU^{VI}$	4		1624 vs	1406 m 1360 s	264	1175	1304 s, 922 s, 603 m, 555 vs, 535 s, 413 m
Fe^{III}	1	1720 s	1580 m	1465 m 1400 s	180	1010	1435 w, 1385 m, 1335 m, 1250 s, 1210 s, 970 s, 910 s, 750 s, 680 m, 620 m, 580 s, 510 m, 490 s
Fe^{III}	0	—	1620 vs	1435 s	185	1128	1420 vs, 1324 s, 997 m, 849 m, 814 m, 572 w
Co^{III}	3	—	1590 vs	1382 s	208	1110	1327 m, 1242 m, 1222 m, 1027 m, 987 m, 951 m, 930 m, 910 m, 874 w, 791 m, 734 m, 637 w, 467 s
Ni^{III}	3	1720 w	1590 vs	1404 s	186	1107, 1122	1326 m, 1288 w, 1232 vs 1220 vs 1004 m, 983 m, 972 m, 914 m, 762 w, 600 m, 550 s, 478 m, 450 w, 412 m

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*Abbreviations: vs, very strong; s, strong; m, medium; and w, weak.

TABLE 2. Frequencies of the Absorption Maxima at 400-650 cm^{-1} in the IR Spectra of Metal Salts of Aminotriacetic Acid*

M	n	δM—O and deformation vibrations, cm^{-1}	$\nu_{M \leftarrow N}$, cm^{-1}	Other frequencies, cm^{-1}
H_3				
Li_3				
Na_3				506, 520, 534, 583
K_3				
B	0	452 m	519 vs	649 vs
Al	2	461 w	545 w	632 w
Ga	2	482 w	517 m, 528 m	564 vs 623 s
In	2		545 w	619 w
Tl	2		524 m	
La^{III}	3		494 m	562 m
Ce^{III}	3	482 m	541 w	580 vw
Nd^{III}	3	482 w	545 w	613 vw
$ClZr^{IV}$	3	483 m	543 m	604 vw, 652s
$HOPb^{IV}$	2		529 m	
Bi^{III}	3		507 w	559 m 615 m
Cr^{III}	3		545 w	618 w
$HOOU^{VI}$	4		535 m	555, 603w, 616 s
Fe^{III}	1	485 w	503 m	
			524 s	572 vw
Co^{III}	3	467 w	539 w	637 vw
Ni^{III}	3	450 vw		
		478 vw	550 m	600w

*Abbreviations: s is strong, m is medium, w is weak, and vw is very weak.

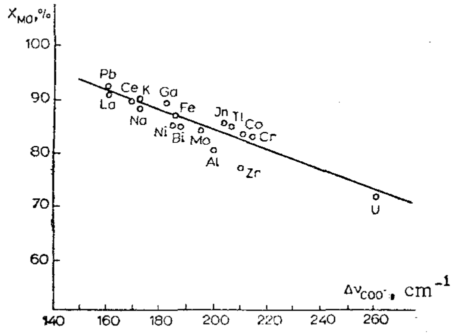

Fig. 1. Dependence between X_{MO} and $\Delta\nu COO^-$.

The absorption bands of the carboxyl groups in the IR spectra of aminotriacetic acid (III) and its salts are divided into three types: 1) $>NCH_2COOH$ (1700-1750 cm^{-1}),* 2) $>\overset{+}{N}CH_2COO^-$ (1620-1630 cm^{-1}), and 3) $>NCH_2COO^-$ (1535-1575 cm^{-1}) [11, 22]. The intensities of the latter two maxima are approximately identical and exceed the intensity of the absorption band of the un-ionized COOH group by a factor of about three. The difference between the frequencies of bands of the latter two types (35-55 cm^{-1}), which pertain to the absorption of the un-ionized carboxyl group in the α-amino acids, is explained by the large inductive effect of the positively charged nitrogen atom, which leads to an increase in the order of the C=O bond in a carboxyl group of the $>\overset{+}{N}CH_2COO^-$ type [22].

Spectroscopy and calculations demonstrated that the bond between the metal and the carboxyl groups in most of salts III is ionic, while the metal—nitrogen bond is to a considerable degree covalent or has donor-acceptor character [13-15, 20, 21].

We have studied the IR spectra of anhydrous I and their hydrates and of III itself and its salts with alkali metals (Li, Na, K) in the region of KBr and NaCl prisms (Tables 1 and 2).

To solve the problem facing us, the vibrations of the ionized and un-ionized carboxyl groups [23] (Table 1), which appear at 1350-1765 cm^{-1}, are of the greatest interest.

The C=O stretching vibrations in free crystalline III are observed at 1728 cm^{-1} for all three carboxyl groups. Transition from III to its trilithium, trisodium, and tripotassium salts leads to the disappearance of this band and to the appearance of $\nu_{as}COO^-$ bands at 1578-1665 cm^{-1} and ν_sCOO^- bands at 1403-1407 cm^{-1}

It is known [23] that the position of the $\nu_{as}COO^-$ band indicates the character of the bond between the metal and the COO^- group. Compounds with a predominantly ionic COO—M bond (M = Na, Ca, etc.) absorb at 1510-1550 cm^{-1}, while compounds with a predominantly covalent bond character (M = Cr^{III}, $HOOU^{VI}$, etc.) at 1630-1650 cm^{-1}. When M = B, Si, the COO — M bond has covalent character ($\nu_{as}COO^-$ 1728 cm^{-1}). The difference between $\nu_{as}COO^-$ (1510-1650 cm^{-1}) and ν_sCOO^- (1300-1450 cm^{-1}) — $\Delta\nu COO^-$ — serves

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*According to our data, the absorption bands of $>NCH_2COOB<$ and $>NCH_2COOSi\lessdot$ are also situated in this region.

as a measure of the covalent character of the $COO^- - M$ bond in salts of the carboxylic acids [23, 24]. This value is 177-187 cm^{-1} for the ionic bond (the trisodium and tricalcium salts of III), as compared with $\Delta\nu COO^- > 225$ for a covalent bond.

As the $\Delta\nu COO^-$ value increases and, consequently, the ionic character of the M−O bond increases, the investigated compounds can be arranged in the following order of change in M (the degree of ionic character of the M−O bond increases):

$$B < Si < HOOU^{VI} < ClZr^{IV} < Cr^{III} < Co^{III} < Tl^{III} < In^{III} < Al <$$
$$< HOOMo^{VI} < Li < Bi < Ni^{III} < Fe^{III} < Ga < Na < K < Ce^{III} < HOPb^{IV} < La$$

For comparison, we calculated the degree of ionic character of the M−O (X_{MO}) bond in the investigated compounds by the method in [25] assuming that $\nu_{as}COOM$ depends only on the polarity of the M−O bond. According to these data, the degree of ionic character increases in the following order:

$$B < Si < HOOU^{VI} < ClZr^{IV} < Li < Al < Cr^{III} < Co^{III} < In^{III} < Tl^{III} <$$
$$< HOOMo^{VI} < Bi < Ni^{III} < Fe^{III} < K < Na < Ga < Ce^{III} < HOPb^{IV} < La$$

Both of the orders presented above are basically identical.

A comparison of the ionic character of the M−O bond (X_{MO}), calculated according to the method in [25, 26], with $\Delta\nu$ (see Fig. 1) attests to the linear dependence between them:

$$X_{MO} = 124.6 - 0.206\Delta\nu$$

This confirms that the $\Delta\nu$ values actually characterize the degree of ionic character of the M−O bonds.

In compounds with $M = La^{III}$, $HOPb^{IV}$, and Ce^{III}, the bond between atom M and the COO^- group is primarily ionic. The M−O bond in compounds with $M = HOOU^{VI}$, Tl^{III}, and $ClZr^{VI}$ has predominantly covalent character.

As the atomic number of metal M in a given group of the periodic system increases, $\Delta\nu_{as}COO^-$ in the spectra of I is shifted to the long-wave region. Thus, for example, for I, in which M is a group III metal, it decreases from 1760 cm^{-1} (M = B) and 1600 cm^{-1} (M = Al) to 1586 cm^{-1} (M = Tl).* The ionic character of the M−O bond increases in the same sequence in this case, and the strength of the $M \leftarrow N$ bond decreases. In accordance with this shift to the long-wave region of $\nu_{as}COO^-$, the stability constants of the neutral chelate salts of III also decrease [11].

The $\nu_s COO^-$ band is usually also shifted to the low-frequency region as the atomic number of metal M in a given group of the periodic system increases. Thus, for example, in the case of group III metals, it decreases regularly from 1400 cm^{-1} (M = Al) to 1380 cm^{-1} (M = Tl) or from 1420 cm^{-1} (M = Sc) to 1406 cm^{-1} (M = La).

The presence of one $\nu_{as}COO^-$ band indicates equivalent bonding with the metal of all three carboxyl groups. One $\nu_{as}COO^-$ band is observed in the spectra of all of the studied I (except for $M = Bi^{III}$ and Fe^{III}). According to the literature data [13], double $\nu_{as}COO^-$ bands are contained in the spectra of compounds with M = Y, Pr, and Nd. However, this band is not in all cases so narrow that one might with confidence conclude that all three COO^- groups are equivalent. In I with $M = Bi^{III}$ and Fe^{III}, the $\nu_{as}COO^-$ band is split into two bands (Table 1), which indicates the nonequivalence of the bonds between the metal and the COO group.

Two $\nu_s COO^-$ bands at 1360-1450 cm^{-1} (Table 1) are observed in the spectra of I with M = Al, Y, Ce^{III}, $ClZr^{IV}$, and $HOOU^{VI}$. This, in conjunction with a broad $\nu_s COO^-$ band, may also indicate the nonequivalence of the bonds of all three carboxyl groups with the metal. These data make it possible to propose that the above-indicated compounds with $M = Fe^{III}$, Bi^{III}, La, Ce^{III}, Y, Pr, Nd, $ClZr^{IV}$, and $HOOU^{VI}$ may have a polymeric structure.

At the same time, the spectra of the hydrates of I with $M = Ce^{III}$, Nd, $ClZr^{IV}$ contain, in addition to a $\nu_{as}COO^-$ band at 1565-1620 cm^{-1}, still another $\nu_{as}C=O$ band at 1738-1763 cm^{-1}, which indicates either the covalent character of one of the M−O bonds or, what is more likely, the presence of a free carboxyl group, i.e., a structure of the II type.

In the case of this structure, a band of the stretching vibrations of a coordinately bonded carboxyl group should be observed in the spectra. The band at ~1380-1410 cm^{-1}, which is observed in the spectra of I with $M = Ce^{III}$, $ClZr^{IV}$, and Ni^{III}, apparently corresponds to it.

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*When M = Ga, however, $\nu_{as}COO^-$ deviates from this dependence (1576 cm^{-1}).

In correspondence with this, hydrates of this type (for example, trihydrates with M = La, Pr, Nd [13]) lose the last water molecule with difficulty during thermal dehydration, and two intense bands of stretching vibrations are observed in their spectra near 3450 and 3100 cm^{-1} [13].

The presence of only one $\nu_{as}COO^-$ band and one $\nu_s COO^-$ band in the spectra of I with M = Sc, La, and Nd (anhydrous compounds), Al, Ga, In, Tl, PbOH (dihydrates), Co, Cr, Nd, Sm (trihydrates), Y, Yb (tetrahydrates) and Pr (pentahydrate) enables one to speak with confidence regarding the equivalent character of all three COO groups in the molecules and to formally assign the metalloatrane-3,7,10-atom M to them.

The ν_s and $\nu_{as}COO^-$ bands do not appear in the spectrum of I with M = B. This is evidence that this compound does not have salt-like character. The presence of a $\nu C = O$ band at 1764 cm^{-1} in its spectra indicates that it can, with complete foundation, be called boratrane-3,7,10-trione, and the $\overleftarrow{B(OCOCH_2)_3N}$ structure can be assigned to it. Similar phenomena are observed in the spectrum of 1-acetoxysilatrane-3,7,10-trione ($\nu C = O$ 1730 cm^{-1}).

The absorption bands at 1020-1220 cm^{-1}, which are often of low intensity, correspond to the C−N stretching vibrations in aliphatic amines [14, 27]. A characteristic absorption band at 1105-1145 cm^{-1} (in some cases it is split into two bands), which is usually of low intensity, is found in this interval in the spectra of all of the substances that we studied and in the spectra of the tripotassium and trisodium salts of III. It can therefore be assigned with confidence to the C−N stretching vibrations. Other investigators [11, 14] also give the same assignment of this band in the spectra of neutral salts of III. In this case, it is noted [11] that the shift of the $\nu C-N$ band to the low-frequency region is linked to an increase in the stability constant of the complex, which can be explained by weakening of the C−N bond due to strengthening of the adjacent $N \rightarrow M$ bond. A quite considerable (up to 45 cm^{-1}) shift of $\nu C-N$ to the low-frequency region as compared with the position of this band in the spectra of the trisodium and tripotassium salts of III (1140-1144 cm^{-1}) is observed in the spectra of all of the studied I and their hydrates. This indicates the formation of a coordinated $M \leftarrow N$ bond in I that has $\nu C-N$ values of 1100-1130 cm^{-1}. It is interesting that the maximum (by more than 30 cm^{-1}) shift of the $\nu C-N$ band is observed in the spectra of I that contain the most electronegative atoms (M = Fe, Co, Ni, Bi, Cr, HOPb).

The presence of a coordinated $M \leftarrow N$ bond in I and in their hydrates is also confirmed by the considerable shift to the high-frequency region of the $\nu C-H$ bands, as compared with the spectrum of the tripotassium salt of III. In the analogous (to I) chelate salts of aminodiacetic acid, the increase in the ν_{C-H} frequencies is accompanied by a decrease in the $\nu N-H$ values, which is also caused by coordination of the M and N atoms [23].

The first question that arises in an analysis of the IR spectra of the investigated compounds at 400-700 cm^{-1} is relative to the assignment of the frequency ($\nu M \leftarrow N$) of the coordinate $M \leftarrow N$ bond. The presence of an $M \leftarrow N$ donor-acceptor bond in the analogs of I − metalloatranes $\overleftarrow{RM(OCH_2CH_2)_3N}$ − is proved convincingly by measurement of their dipole moments and is confirmed by the IR and PMR spectra [28]. The IR spectra of silatrane $\overleftarrow{RSi(OCH_2CH_2)_3N}$ contain an absorption band at ~570 cm^{-1}, which is presumably related to the $\nu Si \leftarrow N$ vibrations [27]. The bands at 570-600 cm^{-1} [28] or at 280-420 cm^{-1} [29, 30] in the spectra of the chelate salts of glycine and alanine are ascribed to the stretching vibrations of the $M \leftarrow N$ coordinate bond. It was also noted in [29, 30] that, because of the relatively great mass of the metal atom and the low stability of the $M \leftarrow N$ coordinate bond, the $\nu M \leftarrow N$ stretching vibration should appear in the low-frequency region. The frequencies near 500 cm^{-1} [27] or at 400-500 cm^{-1} [14] are most commonly assigned to this vibration. An examination of the low-frequency region of the spectra of I, III, and salts with alkali metals (Table 2) makes it possible to hypothetically assign the absorption band of low or medium intensity at 500-550 cm^{-1} to the vibrations of the coordinate bond. The band of medium intensity at 450-500 cm^{-1} is apparently related to the $\delta M-O$ deformation vibrations [30] and the vibrations of the atrane skeleton.

EXPERIMENTAL

The spectra were measured with an IKS-14 spectrophotometer. To prepare the samples (~1-mm-thick pellets), a fine powder of the substance under investigation was mixed thoroughly in a vibration mill with dried (at 100°) KBr powder that had been sifted through a sieve with 1460 holes/cm^2 (in ratios from 1 : 100 to 1 : 1000), and the mixture was compressed in vacuo at 9000 kg/cm^2. The concentration of the substance during recording of the spectrum in the region of an NaCl prism was $2 \cdot 10^{-2}$ M, as compared with $4 \cdot 10^{-2}$ M in the region of a KBr prism. The methods used to synthesize the investigated metalloatrane-3,7,10-triones were previously described in [2-4].

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