A. I. GRIGOR'EV, N. M. PRUTKOVA, N. D. MITROFANOVA,

L. I. MARTYNENKO, Academician Vikt. I. SPITSYN

1965

SovietRxiv

Abstract

Full Text

CHEMISTRY

A. I. GRIGOR' EV, N. M. PRUTKOVA, N. D. MITROFANOVA,
L. I. MARTYNENKO, Academician Vikt. I. SPITSYN

INVESTIGATION OF NEUTRAL IMINODIACETATES OF CERTAIN METALS BY INFRARED SPECTROSCOPY

The study of complex compounds of iminodiacetic acid (IMDA) by IR spectroscopy is of special interest in connection with the investigation of the nature of the metal—nitrogen bond. Although IMDA derivatives are weaker complexes than the corresponding derivatives of ethylenediaminetetraacetic and nitrilotriacetic acids ($^{1-5}$), and the metal—nitrogen bond in them is probably also weaker, iminodiacetates are of interest in that they invariably contain a bond between nitrogen and hydrogen. At the same time it is known that a shift of the frequencies of the stretching vibrations of N—H bonds toward the region of lower frequencies is a good criterion for the formation of a covalent bond by nitrogen. The magnitude of the frequency shift can be used for a comparative estimate of the strength of such bonds in analogous compounds of different metals. From what has been said it is clear that, in studying the IR spectra of complex iminodiacetates, comparison of the frequency values of the stretching vibrations of the N—H, C—H, and also C—N bonds (^{5}) is of definite interest.

In the present work the IR absorption spectra of the following solid IMDA derivatives were studied: H_2Z, KHZ, K_2Z, MgZ, CaZ, SrZ, BaZ, Al_2Z_3, La_2Z_3, Y_2Z_3, Sc_2Z_3. In addition, solid deuterated compounds D_2Z^*, KDZ^*, and K_2Z^{**} were synthesized. Investigation of their spectra is necessary for the correct assignment of the stretching-vibration frequencies of the N—H and C—H bonds.

The preparations KHZ and K_2Z were prepared by adding to solid H_2Z solutions containing, respectively, one and two equivalents of KOH. The KHZ solutions (pH 6.4) and K_2Z solutions (pH 10.2) were evaporated under vacuum in order to avoid their absorption of CO_2 from the air. Neutral iminodiacetates were obtained by mixing solutions of equivalent amounts of K_2Z and $Me^{II}Cl_2$, where $Me^{II} = Mg, Ca, Sr, Ba$: $Me^{II}Cl_2 + K_2Z \rightleftarrows Me^{II}Z + 2KCl$, or $Me^{III}Cl_3$, where $Me^{III} = Al, La, Y, Sc$: $2MeCl_3 + 3K_2Z \rightleftarrows Me_2^{III}Z_3 + 6KCl$. The concentration of the solutions and isolation of the solid preparation were carried out in the same way as in the case of KHZ and K_2Z. Thus, in accordance with the reaction equations, the preparations of solid iminodiacetates were obtained in admixture with KCl, which, however, could not affect the character of the IR spectra.

Neutral beryllium iminodiacetate was not obtained. This is apparently a very unstable compound; therefore in neutral and alkaline media it is completely hydrolyzed with formation of a precipitate of $Be(OH)_2$, while in an acid medium it forms the salt $Be(HZ)_2$, which has no complex character.

The composition of the solid iminodiacetates obtained was determined as follows. The metal content was estimated complexometrically. The amount of KCl in the mixture was established by determining the amount of Cl′ (gravimetrically, as AgCl). The amount of IMDA was calculated from the difference in weights of the anhydrous preparation, the metal, and KCl. As an example, in Table 1 the results of analysis of the preparations La_2Z_3, Y_2Z_3, Sc_2Z_3, and Al_2Z_3 are given. Dehydration of the preparations was carried out on a continuously weighing balance; constant weight and complete dehydration were attained at 250–270°.

Table 1

Composition of preparations of normal iminodiacetates (wt.%)

Formula of the crystalline hydrate	Me found	Me calculated	Z found	Z calculated	KCl found	KCl calculated	H_2O found	H_2O calculated
$La_2Z_3 \cdot 2H_2O$	24.19	24.05	33.79	34.06	39.02	38.75	3.00	3.14
$Y_2Z_3 \cdot 2H_2O$	16.71	16.87	37.62	37.30	42.07	42.33	3.06	3.48
$Sc_2Z_3 \cdot H_2O$	9.74	9.51	41.03	41.49	47.25	47.10	1.98	1.90
$Al_2Z_3 \cdot 3H_2O$	5.69	5.70	41.31	41.50	47.31	47.10	5.49	5.70

For the preparation of deuterated preparations, heavy water with a D_2O content of 99.7% was used. D_2Z^* was obtained by heating H_2Z with an excess of D_2O in an ampoule at 100°. Deuterated KDZ* and K_2Z^* were prepared by dissolving KHZ and K_2Z in D_2O, followed by heating the solutions in an ampoule on a water bath. Concentration of the solutions and isolation of the preparations in the solid state were carried out in vacuo.

---

* The asterisk here and below means that the hydrogen attached to the nitrogen of IMDA has been replaced by deuterium.

To obtain the IR spectra, the crystalline substances were suspended in vaseline oil or in hexachlorobutadiene. The spectra were recorded with a double-beam IKS-14 spectrometer with LiF prisms (2000-3400 cm^{-1}) and NaCl prisms (1000-1800 cm^{-1}). The IR absorption spectra are presented in Fig. 1. The frequency values of the most important absorption bands are given in Table 2. Examination of the IR spectra obtained for iminodiacetates shows the following.

Table 2

Most important frequencies of stretching vibrations in the IR spectra of IMDA derivatives (cm^{-1})

Compound	νN–H (N–D)	νC–H	νas C–O	νs C–O	νC–N
H_2Z	3098	3026, 2968	1708, 1590	1395, 1240	1071, 1041
D_2Z*	2280	3024, 3008, 2972	1709, 1592	1396, 1242	1062, 1040
KHZ	3040-2968	2776	1620	1376	1092, 1072
KDZ*	2245, 2159	2998, 2942	1620	1374	1073, 1046
K_2Z	3326	2940, 2797	1592	1378	1140, 1122
K_2Z*	2464	2930, 2802	1590	1394	1130, 1120
BaZ	3304	2868	1587	1378	1126
SrZ	3292	2876	1590	1373	1122
CaZ	3280	2888	1596	1366	1118
MgZ	3272	2916	1606	1362	1115
La_2Z_3	3260	2917	1592	1363	1116
Y_2Z_3	3252	2921	1588	1362	1117
Sc_2Z_3	3256	2919	1589	1363	1114
Al_2Z_3	3220	2926	1638	1358	1108

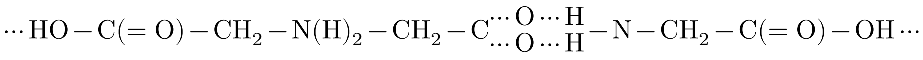
In the spectrum of the crystalline salt K_2Z, the frequencies of the stretching vibrations of the C–O bonds of the ionized carboxyl groups have the same values as the corresponding vibrations in the spectra of potassium nitrilotriacetate or potassium ethylenediaminetetraacetate (1, 4, 5). In the spectra of these compounds the frequencies of the stretching vibrations of the C–N bonds (1140 cm^{-1}) are also practically identical. In the region 2500-3500 cm^{-1}, three rather intense bands appear in the spectrum of K_2Z (2940, 2797, and 3326 cm^{-1}). As follows from Fig. 1, the positions of two bands lying in the region of lower frequencies do not change on passing to the spectrum of the deuterated salt K_2Z*. The posi-

3326 cm^{-1} in the spectrum of K_2Z corresponds to the band at 2464 cm^{-1} in the spectrum of K_2Z^*. Thus, the latter band may be assigned to the stretching vibration of the N–H bond, and the first two to vibrations of C–H bonds. Their values also differ little from the frequency values of the corresponding bands in the spectrum of crystalline potassium nitrilotriacetate (2958 and 2800 cm^{-1}) (5).

As in the spectrum of acid potassium nitrilotriacetate, in the spectrum of KHZ both bands of the stretching vibrations of C—H bonds are shifted into the region of higher frequencies, as compared with their position in the spectrum of the normal potassium salt. At the same time, the band of the stretching vibrations of N—H is shifted into the region of lower frequencies and is superimposed on the bands of the stretching vibrations of C—H bonds. Both groups of bands are clearly separated in the spectrum of KDZ*. As is seen from Fig. 1, in the region of stretching vibrations of N—D bonds two bands appear, evidently corresponding to the symmetric and antisymmetric vibrations of two N—D bonds in KDZ*. The band of stretching vibrations of C—N bonds, on going from the normal potassium salt to the acid salt, shifts into the region of lower frequencies. The band of the symmetric stretching vibration of C—O does not change its value in this process. The band of the antisymmetric vibration of these bonds shifts somewhat into the region of higher frequencies, apparently owing to an induction effect associated with the appearance of a positive charge on nitrogen (5).

Fig. 1. IR absorption spectra of iminodiacetic acid and its derivatives (see Table 2)

The frequencies of the stretching vibrations of C—H, C—N, and N—H bonds in the spectrum of H_2Z and D_2Z^* have approximately the same values as in the spectra of the acid salts KHZ and KDZ*. On the contrary, in the region of the stretching vibrations of C—O bonds a substantial difference is observed here. In this region of the spectra of H_2Z and D_2Z^* there are two pairs of intense bands: 1708, 1240 and 1590, 1395 cm^{-1}. The first pair of bands can belong only to the nonionized carboxyl group $\left|-\mathrm{C}^{=\mathrm{O}}_{\backslash\mathrm{OH}}\right|$, the second to the carboxyl ion $\left|-\mathrm{C}^{=\mathrm{O}}_{\backslash\mathrm{O}}\right|$. Thus, the spectrum of H_2Z differs substantially from the spectrum of nitrilotriacetic acid, where only bands corresponding to nonionized carboxyl groups are present. The structure of IMDA can be represented by the following structural formula:



$$\cdots\mathrm{HO}-\mathrm{C}(=\mathrm{O})-\mathrm{CH_2}-\mathrm{N(H)_2}-\mathrm{CH_2}-\mathrm{C}^{\cdots\mathrm{O}\cdots\mathrm{H}}_{\cdots\mathrm{O}\cdots\mathrm{H}}-\mathrm{N}-\mathrm{CH_2}-\mathrm{C}(=\mathrm{O})-\mathrm{OH}\cdots$$

$$\mathrm{CH_2}, \qquad \cdots\mathrm{O}=\mathrm{C}=\mathrm{O}\cdots$$

In the region 2400-2600 cm^{-1} in the spectrum of H_2Z, as also in the spectrum of nitri-

of nitrilotriacetic acid, bands appear which, evidently, belong to the stretching vibrations of the OH groups of carboxyl groups forming hydrogen bonds.

In the spectrum of most IDA salts (normal salts) shown in Fig. 1, the frequencies of the C—O stretching vibrations have the same values as in the spectrum of K_2Z. Consequently, the Me—O bonds in these compounds are purely ionic in character. Only in the spectra of MgZ and Al_2Z_3 (as also in the spectra of the corresponding nitrilotriacetates) does the frequency of the C—O bond stretching vibration prove to be shifted into the region of higher frequencies, which apparently indicates the emergence under these conditions of more or less covalent Me —O bonds. In the spectra of normal iminodiacetates, only one band is observed in the region where C—H stretching vibrations appear. In the spectrum of the most ionic BaZ it has the value 2868 cm^{-1}, which is almost the arithmetic mean of the values of the two ν_{C-H} bands in the spectrum of K_2Z (2870 cm^{-1}).

The frequencies of the C—H stretching vibrations in the spectra of all iminodiacetates presented in Fig. 1 are shifted, in comparison with the frequency in the spectrum of BaZ, into the region of higher frequencies. At the same time, the magnitude of the shift increases in the series of compounds Ba, Sr, Ca, Mg from Ba to Mg and in the series of compounds La, Y, Sc, Al from La to Al. The maximum shift is observed for compounds of the elements of the third group (\$ 60 $cm^{\{-1\}}$). It is characteristic that this maximum shift is smaller than the corresponding displacement in complex nitrilotriacetates (70- 1}\$).

In accordance with the displacement of the ν_{C-H} bands, the ν_{C-N} bands in the spectra of the normal salts are shifted somewhat into the region of lower frequencies. Such behavior of the ν_{C-H} and ν_{C-N} frequencies shows that covalent coordination Me—N bonds arise in complex iminodiacetates, although apparently weaker than in the nitrilotriacetates of the same metals.

The possibility of formation of covalent coordination Me—N bonds is confirmed by the simultaneous change in the frequencies of the N—H stretching vibrations. In the same order in which the frequencies of the C—H stretching vibrations increase in the spectra of the series of normal iminodiacetates, the frequencies of the N—H stretching vibrations decrease. In the case of Al_2Z_3 this effect of lowering the ν_{N-H} frequency reaches 90 cm^{-1}. Although this value is considerably smaller than the shift of the ν_{N-H} frequencies attained in the spectra of the compounds KHZ and H_2Z, it is in itself very large and indicates the formation of a strong covalent bond at the expense of the unshared electron pair of the nitrogen atom. It should be noted that this effect of frequency shift cannot in any way be attributed to the formation of hydrogen bonds between nitrogen and carboxyl oxygen, since the negative charges on the oxygen atoms of the carboxyl groups in the series of iminodiacetates Ba—Mg and La—Al can only decrease.

Moscow State University
named after M. V. Lomonosov

Received
13 XI 1964

REFERENCES

1. D. T. Sawyer, P. J. Paulsen, *J. Am. Chem. Soc.*, **80**, 1597 (1958).
2. D. T. Sawyer, P. J. Paulsen, *J. Am. Chem. Soc.*, **81**, 816 (1959).
3. D. T. Sawyer, J. M. McKinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).
4. N. D. Mitrofanova, L. I. Martynenko, A. I. Grigor' ev, *ZhNKh*, **9**, 320 (1964).
5. A. I. Grigor' ev, N. D. Mitrofanova, L. I. Martynenko, *Zhurnal neorganicheskoi khimii*, **10**, No. 3 (1965).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.