Reports of the Academy of Sciences of the USSR

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1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 159, No. 4

PHYSICAL CHEMISTRY

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SOME FEATURES OF THE INFRARED ABSORPTION SPECTRA OF VANADYL COMPOUNDS WITH CARBOXYLIC ACIDS

(Presented by Academician V. I. Spitsyn, June 24, 1964)

It is known that alkanoates (of the acetate type) of divalent copper, which, like VO(II), has one unpaired electron at the $3d$ level, contain as a structural element of the crystal a dimeric molecule with a very short (2.64 Å) Me—Me distance. Such a structure makes possible the formation of a δ-bond Cu—Cu through overlap of the $d_{x^2-y^2}$ orbitals, as a result of which the magnetic moment proves to be substantially below the theoretical value (^{1,2}). The structural features are manifested not only in the anomaly of magnetic susceptibility, but also in e.p.r. spectra (^{3}), as well as in the infrared absorption spectra.

Kuroda, who investigated the infrared spectra of copper compounds with normal fatty acids (^{4}), noted in particular that the bands corresponding to the antisymmetric stretching vibrations of the carboxyl group $\nu_a(\mathrm{COO}^-)$ for solid salts lie somewhat higher than for the sodium salts of the corresponding acids. The frequency $\nu_a(\mathrm{COO}^-)$ of solid copper formate, which has a magnetic moment close to the theoretical value, is comparable with the frequency $\nu_a(\mathrm{COO}^-)$ of sodium formate*. In dioxane solutions, for all compounds, especially copper formate, a considerable short-wavelength shift was found, accompanied by a decrease in the magnetic moment. According to Martin (^{6}) and Kuroda (^{4}), both of these phenomena are explained by formation of a dimeric structure upon dissolution of Cu formate and, in general, by an increase in spin–spin interaction for all the compounds considered in the dissolved state.

Obviously, such an explanation is not unambiguous. It is clear that a decrease in the magnetic moment is connected with a change in the character and degree of exchange interactions between paramagnetic ions. However, if in the formate one may assume an increase in exchange interaction as a result of the approach of Cu(II) ions in comparison with the crystalline state (the Cu—Cu distances in the crystal are 5.8 and 6.2 Å), it is difficult to allow a further approach of the ions in acetate. It seems probable to us, especially in the latter case, that—analogously to copper stearate (7)—dimeric or polymeric associations with bridges of dioxane molecules are formed, through which exchange interactions are effected.

Further, Kuroda regards the somewhat higher values of the frequencies $\nu_a(COO^-)$ for solid Cu salts as compared with Na salts as anomalous, and the short-wavelength shift upon dissolution as an intensification of the anomaly. According to studies (8–11), however, the indicated short-wavelength shift is typical of compounds with a more covalent Me—carboxylate-ion bond than in Na salts. Comparison of the ionic radii of Cu(II)—0.69 Å and Na(I)—0.96 Å, and also of the ionization potentials of Cu(I) and Na^0—20.22 and 5.14 eV, respectively, permits the qualitative conclusion that in Cu(II) the tendency toward formation of a covalent bond is greater than in Na(I). In in such a case one may regard the frequency $\nu_a(COO^-)$ of Cu salts in solution as normal, and the long-wavelength shift for solid salts as anomalous, due to structural superpositions. In this case, an increase in the electron density at Cu(II) as a result of overlap of the $d_{x^2-y^2}$ orbitals can indeed cause a stronger displacement of the electrons participating in the formation of the Me—carboxylate-ion bond toward the carboxylate ion, i.e., an increase in the ionic character of the bond. Then, according to (8–11), the frequency $\nu_a(COO^-)$ should decrease.

Earlier we proposed that the anomalous magnetic properties of certain vanadyl alkanoates are also due to features of their structure (12). Moreover, the nature of the temperature dependence of the magnetic susceptibility and of the exchange integral, as well as certain physical properties, made it possible to prefer not a dimeric structure, but a polymeric one. The present work discusses certain features of the IR absorption spectra of vanadyl formate, benzoate, and *o*-iodobenzoate, whose magnetic properties we have already studied (12), as well as of vanadyl compounds with acetic acid, some of its homologs, and mono-, di-, and trichloro derivatives*. Table 1 gives the wave numbers of the frequencies $\nu_a(COO^-)$ for vanadyl compounds, the corresponding sodium and some copper salts, and the wave numbers of the frequencies of the stretching vibrations $\nu(V{=}O)$.

Table 1

Compound	$\nu_a(COO^-)$, cm^{-1}	$\nu(V{=}O)$, cm^{-1}	Source
$VO(HCOO)_2 \cdot 0.5H_2O$	1572	990	
$Cu(HCOO)_2 \cdot 4H_2O$	1565		(4)
$Na(HCOO) \cdot 2H_2O$	1590		(5) and our data
$VO(C_6H_5COO)_2$	1582	892	

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* According to our data, and also according to (5), the frequency $\nu_a(COO^-)$ for sodium formate is 1590 cm^{-1}, and not 1567 cm^{-1}, as Kuroda assumes.

Compound	$\nu_a(COO^-)$, cm^{-1}	$\nu(V{=}O)$, cm^{-1}	Source
$Na(C_6H_5COO)$	1600		(13)
$VO(O{-}J{-}C_6H_4COO)_2$	1567	894	
$Na(O{-}J{-}C_6H_4COO)$	1594		
$VO(CH_3COO)_2$	1518	898	
$Cu(CH_3COO)_2 \cdot H_2O$	1602		(4)
$Na(CH_3COO)$	1580		(14)
$VO(ClCH_2COO)_2$	1550	898	
$Na(ClCH_2COO)$	1592		
$VO(Cl_2CHCOO)_2$	1582	898	
$Na(Cl_2CHCOO)$	1628		
$VO(Cl_3CCOO)_2$	1593	897	
$Na(Cl_3CCOO)$	1664		
$VO(C_2H_5COO)_2$	1523	890	
$Cu(C_2H_5COO)_2$	1589		(4)
$Na(C_2H_5COO)$	1565		(14)
$VO(C_3H_7COO)_2$	1523	890	
$Na(C_3H_7COO)$	1565		(14)
$VO(C_8H_{17}COO)_2$	1530	890	
$VO(C_8H_{17}COO)_2$	1518		
$Na(C_8H_{17}COO)$	1567		

As indicated in (15,16), in vanadyl compounds the frequency of the stretching vibration ν(VO), while varying depending on the type of ligand or solvent (for solutions), remains for most known compounds within a narrow interval—965-995 cm^{-1}. It is not difficult to see that, among the compounds we studied, only for vanadyl formate does the frequency ν(VO) correspond to the usual value; in all the other cases a strong long-wavelength shift ($\Delta\nu$) of about 100 cm^{-1} is observed. The large absolute magnitude and the nearly coincident values of $\Delta\nu$ suggest that it is caused by a structural reason common to all the compounds. One may assume the formation of a single or double additional donor-acceptor bond of V(IV), which has free *d*-orbitals, with unshared electron pairs of the oxygen of another VO grouping, $\overset{-}{V} = \overset{+}{O}V = \overset{+}{O}\overset{-}{V} \equiv \overset{+}{O}$, etc. (but not an increase in the bond multiplicity V=O in vanadyl, since in that case the force constant and, accordingly, the vibration frequency of the bond would increase) (17). Then the frequency ν(VO) may decrease both due to the mass effect and due to a change in the electron density of V(IV) and O(II).

An increase in the effective electronegativity of V(IV) with the formation of an additional bond should cause, to a corresponding degree, a displace-

* The method of their synthesis will be published elsewhere.

the electron cloud in the direction of the oxygen atoms of the (COO^-) group, i.e., an increase in the effective ionicity of the bond of V(IV) with this group. Indeed, as is seen from the data of Table 1, the frequencies $\nu_a(\mathrm{COO}^-)$ are substantially lower than in the corresponding Na compounds for all vanadyl compounds, especially for the compounds with aliphatic acids from acetic acid upward, and for the acetochloro derivatives. On the basis of the values of the ionic radius of V(IV)—0.64 Å—and the ionization potential of V(III)—48 eV—one may assume, in the general case, a strong tendency of V(IV) toward the formation of a covalent bond. It should then be concluded that such large anomalies of the frequencies $\nu_a(\mathrm{COO}^-)$ can be due only to a very substantial redistribution of electron density as a result of an additional donor-acceptor bond, while the bond itself is fairly strong (the latter probably explains the practical insolubility of the compounds in ordinary organic solvents). For comparison we note that the wave numbers of the frequencies $\nu_a(\mathrm{COO}^-)$ in the VO(II) compound with ethylenediaminetetraacetic acid are 1630 cm^{-1} (in D_2O solution, 1620 cm^{-1}) and $\nu(\mathrm{VO})$ is 970 cm^{-1} (the assignment is ours) (11,18).

The assumption of an additional bond

$$\overline{\mathrm{V}} = \overset{+}{\mathrm{O}} \rightarrow \mathrm{V} = \overset{+}{\mathrm{O}} \rightarrow \mathrm{V} = \overset{+}{\mathrm{O}}$$

appears to be a more convincing explanation of the strong exchange interactions between paramagnetic ions in $\mathrm{VO(C_6H_5COO)_2}$ and $\mathrm{VO(O-I-C_6H_4COO)_2}$ (12), and also, probably, in all the other compounds, except vanadyl formate (12), than a scheme of exchange predominantly through a bidentate COO^- ion associated with different VO(II) ions. The indicated bond may serve as a channel through which the density of the unpaired electron from the oxygen atom of vanadyl passes to V(IV) of the neighboring VO ion (19) (because of the multiplicity of the $\mathrm{V} = \mathrm{O}$ bond, the density of the unpaired electron on the oxygen atom must be different from zero). In this case V(IV) exhibits a coordination number of 6, which is highly characteristic of it (15).

The similarity of the magnetic properties of VO(II) and Cu(II) formates (20), as well as the closely coinciding IR spectra—$\nu(\mathrm{COO}^-)$ 1361 and 1366 cm^{-1}, $\delta(\mathrm{C-H})$ 1382 and 1387 cm^{-1} for VO(II) and Cu(II) formates (4), respectively—make it possible to assume for $\mathrm{VO(HCOO)_2 \cdot 0.5H_2O}$ also a planar network structure with exchange interactions in the layers. It is probable that the delocalization of the π-electron cloud, arising from overlap of the $2P_\pi(\mathrm{O})$—$2P_\pi(\mathrm{C})$—$2P_\pi(\mathrm{O})$ orbitals and associated with delocalization of the double bond according to the scheme $-\mathrm{O-CH=O/O=CH-O}-$, is the main cause responsible for the small long-wavelength shift of $\nu_a(\mathrm{COO}^-)$ in comparison with the Na salt and for some diamagnetization of the paramagnetic ions.

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Received
17 VI 1964

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