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Vibrational Spectrum of Solid Sodium Hydrogen Bis(formate). An Unsymmetrical Very Short OH···O Bond in a Complex Containing Spectroscopically Distinct HCO_2^- and HCO_2H Entities

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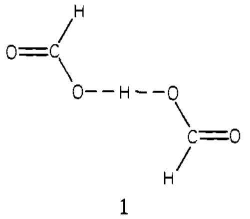
Abstract: The infrared and Raman spectra of solid $NaH(HCO_2)_2$, $NaD(HCO_2)_2$, $NaH(DCO_2)_2$, $NaD(DCO_2)_2$, and $NaH(HCO_2)(DCO_2)$ (an isotopic mixture) have been determined. The infrared spectra show broad intense hydroxyl stretching absorption centered around 1100 cm^{-1} for both OH and OD species. All bands expected for a formate ion moiety and most of those expected for a formic acid moiety appear in both the infrared and the Raman spectrum. The isotopic mixture exhibits (expectedly) all bands shown by $(HCO_2)_2H^-$ and all shown by $(DCO_2)_2H^-$, *but no others* that are distinctly characteristic of the species $[(HCO_2)(DCO_2)H]^-$, even though ca. 50% isotopically mixed complexes are undoubtedly present. The two HCO_2 portions in the complex are not chemically identical, and the hydrogen bond is of the unsymmetrical type O–H···O, as shown also by the ratio $\nu_{OD}/\nu_{OH} \approx 1$. In the solid Na salt the complex does not possess the centrosymmetric C_{2h} structure predicted for it by recent ab intio molecular orbitals calculations.

Compounds with extremely short OHO hydrogen bonds, r(O···O) $\leq$ 2.48 Å, and extremely low OH stretching frequencies, in the range 1200–600 cm^{-1} (very broad IR bands), have been much studied, mainly by diffraction crystallography[1] and infrared spectroscopy.[2,3] Special interest attaches to the symmetry or asymmetry of the hydrogen bond and to the details of the potential energy curve[4] or hypersurface[5] (single-minimum or double-minimum type, barrier height, etc.).

For the simplest possible bis(carboxylate) system, $[(HCO_2)_2H^-]$, in vacuo, a recent ab initio molecular orbitals calculation[6] predicted that the most stable form has the planar centrosymmetric structure **1** (with point group C_{2h}). Structure **3** (also of C_{2h} symmetry) was calculated to be 0.006610 hartrees less stable than **1**. However, a change of the formate vs. formate interplanar angle in **1** from 180° to 90° (by torsion about the OHO axis) gave a loss in stability by only 0.000587 hartrees. Structures **2** and **4**, the unsymmetrical counterparts of **1** and **3**, were found to be of "substantially higher energy" than **1**, but no actual figures were given. Calculations for short OHO bonds in other simple systems repeatedly predicted shallow minima in the potential energy curves ("soft potentials"), implying ready distortability by external electric fields (cf. also results by Ažman, Hadži, and Koller referred to in ref 3). For example, for $H_5O_2^+$ calculations[7,8] predicted that in the most stable form the hydrogen bond is symmetrical, H_2O--H--OH_2 (D_{2d} symmetry). But very little energy is required to displace the bonding hydrogen off center,[8] and when r(O···O) is lengthened the single-minimum potential is gradually replaced[9] by a symmetrical double-minimum potential. $H_3O_2^-$, by contrast, was calculated[8,10] to have an unsymmetrical O–H···O bond in its equilibrium configuration, with r(O–H) in the range 1.09–1.11 Å, r(H···O) 1.34–1.37 Å, r(O···O) 2.45–2.465 Å (complex planar, C_s symmetry); i.e., there is a symmetrical double-minimum potential; but the predicted barrier to interconversion to the mirror image structure (via centrosymmetric [HO--H--OH]$^-$) is very low (0.0002 au). All this suggests that extrapolation for bis(formate) ion from the gaseous[6] to the solid-state structure might be hazardous.



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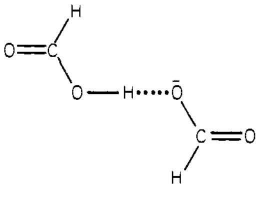

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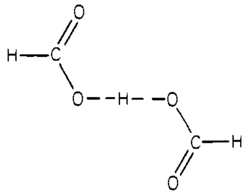

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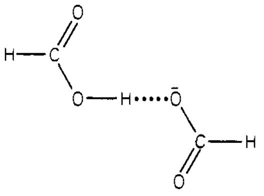

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The only solid bis(formate) to have been reported on so far seems to be the potassium salt. X-ray diffraction crystallography[11] revealed an r(O···O) of 2.44$_7$ Å, i.e., extremely short on the scale of experimental values but longer than the ab initio predicted[6] value of 2.34 Å. Hydrogen atoms were not located. The two HCO_2 moieties in the complex have similar but not identical dimensions; the HCO_2/HCO_2 interplanar angle is 110°, i.e., fairly close to Emsley's[6] "gauche" conformation. The complex may be looked upon as a version of form **1** somewhat distorted by the crystal forces.[6] This interpretation assumes an unsymmetrical single-minimum potential; however, if r(O···O) is less than 2.5

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[1] Very short hydrogen bonds are often referred to as of "type A" if crystallographically symmetrical and of "type B" if crystallographically unsymmetrical: Speakman, J. C. *MTP Int. Rev. Sci. Phys. Chem., Ser. One* **1972**, *11*, 1–31 and much work cited therein.

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Table I. Frequencies of Infrared (IR) and Raman (R) Bands of Solid Sodium Bis(formate) (cm^{-1})[a]

	$(HCO_2)_2H^-$		$(HCO_2)_2D^-$		$(DCO_2)_2H^-$		$(DCO_2)_2D^-$		$HCO_2DCO_2H^-$ [c]
assignment	IR	R	IR	R	IR	R	IR	R	IR
A comb[d]	2949		2948		2919		2917		2951, 2920
N CH st	2902	2902	2899	2900	2184	2185	2183	2184	2902, 2185
A comb[e]					2094	2098	2093	2096	2096
A CH st	2778	2780	2778	2781	2070	2074	2069	2073	2778, 2070
A 2 × CH ip bend	2697	2699	2696	2698	2003	2007	2003	2006	2698, 2005
A 2 × CH op bend								1830	
N C=O st	1755		1716		~1742		~1695		1750[j]
A CO st I		1669		1669		1662		1662	
A CO st I	1626	1640	1626	1641	1619	1626	1617	1626	1621[j]
N CH ip bend	1400[g]	1396	1400	1396	1001↓[h]	~996	1001↓[h]	?[i]	1399,[g] 1006↓[h]
A CH ip bend	1373	1374	1373	1374	1014	1015	1014	1015	1371, 1014
A CO st II	1366	1367	1366	1367	1341	1348	1341	1348	1367, 1342
N C–O st	1316	1324	1316	1322	1305	1317	1305	1317	1310[j]
A CH op bend	1066	1067	1066	1067	916	915	916	917	917
N CH op bend	(1061↓)[h]				903		904		902
A OCO scis	768	767	768	767	759	759	758	759	766, 757
N OCO scis	730	(724)	729		722		721		726[j]
N OD op bend			696	686			690	(680)	
N···A H···O st ?[f]	(465)	450		450		450		450	
N OH st[f]	~1100		~1100		~1100		~1100		

[a] Very weak bands in parentheses; for unassigned Raman frequencies below 300 cm^{-1}, see supplementary material. [b] A = anionic formate, N = neutral formic acid; st = stretching, bend = bending, ip = in-plane, op = out-of-plane, scis = scissoring. Nomenclature for formate ion vibrations as in ref 25a. For CH read CD where appropriate. [c] Quaternary mixture $(HCO_2)_2H^-$ + $(DCO_2)_2H^-$ + $(HCO_2H\cdot)(DCO_2^-)$ + $(DCO_2H\cdot)(HCO_2^-)$. [d] Combination band CO st I + CO st II. [e] Combination band CO st II + OCO scis. [f] Very broad. [g] Frequency of maximum, but band partly inverted. [h] Frequency of minimum of inverted band. [i] Broad weak inflexion. [j] Only one merged band visible (component bands not very narrow).

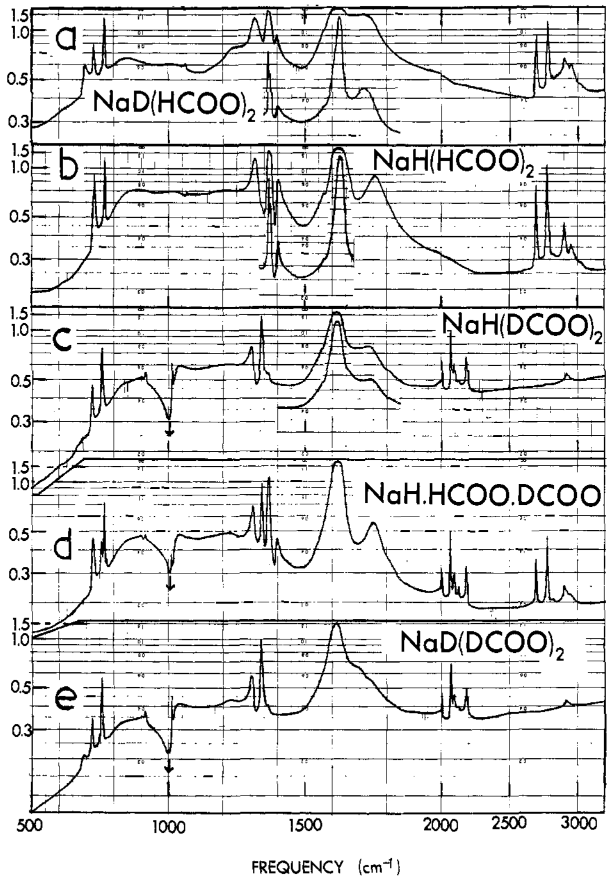

Figure 1. Infrared spectra. Disks in KBr. Disk concentrations not equal; insets obtained with more dilute disks. Arrows indicate fully inverted bands. Spectrum d is of isotopic mixture formed from 1:1 HCO_2H and DCO_2Na. Grating and filter changes at 2000 and 1140 cm^{-1} sometimes cause steps in trace.

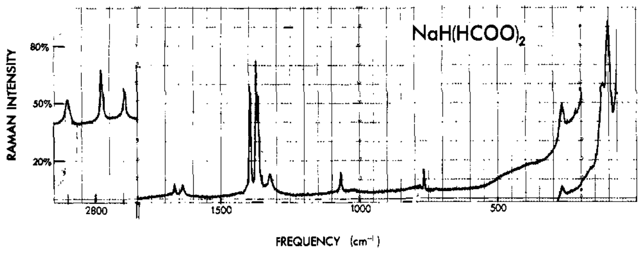

Figure 2. Raman spectrum of neat powder (laser emission line visible at 221.5 cm^{-1}).

Å, it is very seldom possible to distinguish on the basis of diffraction data between an unsymmetrical single- and an unsymmetrical double-minimum potential. This is analogous to the (repeatedly discussed[12]) difficulty with type A salts,[1] which, a priori, may have a symmetrical single-minimum or a symmetrical double-minimum potential. The infrared spectra[3] of $KH(HCO_2)_2$ and $KD(HCO_2)_2$ (remeasured here) have a very broad and very intense hydroxyl stretching band centered around 1400 cm^{-1}. This obliterates many features of interest; in addition, the crystal structure is complicated, with eight formula units in the primitive unit cell; the amount of structural information obtainable from these spectra is therefore severely limited.

Here infrared and Raman spectra are reported for the solid sodium salt in four "homonuclear" isotopic species and for an isotopic mixture containing the "heteronuclear" species $[HCO_2\cdot DCO_2\cdot H]^-$. The spectra are detailed, yet not too complicated to be structurally informative. Though the crystal structure of this (long known[13]) salt is unknown, the frequency of the center of the hydroxyl absorption, ca. 1100 cm^{-1}, corresponds[2b] to r(O···O) no greater than 2.48 Å (probable length ca. 2.45 Å).

Results and Discussion

The infrared spectra obtained are depicted in Figure 1, the Raman spectrum of the parent H_3 complex salt is seen in Figure 2, and band frequencies are listed in Table I.

Main Features of Spectra. The most conspicuous feature in the infrared spectra is the broad intense continuum extending from

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ca. 600 cm^{-1} to at least 1500 cm^{-1}, though the probable onset is ca. 2100 cm^{-1}. In addition to normal upward-pointing bands on top of the plateaus, there are some inverted and some partly inverted bands, typical[14] of "Hadži type ii" spectra[2] of compounds with very short OHO bonds, and due to interaction between an excited continuum state and sharp, discrete excited states.[15] For $NaD(HCO_2)_2$ there appears to be a weak minimum at the center of gravity of the plateau (1100 cm^{-1}), but this may be an accidental consequence of weak bands on top; the other species do not show such a dip. No inverted Raman bands can be seen.

O-Deuteration has relatively little effect on the infrared and even less on the Raman spectra. However, the infrared continua, while essentially unchanged in frequency range, are of considerably lower intensity in the OD salts. The only good infrared band for monitoring the completeness of the deuteration is that in the 1760–1690 cm^{-1} range. In the Raman spectra this frequency is absent. The Raman bands are mostly fairly narrow, but around 450 cm^{-1} there is a broad one, weak for the $(HCO_2)_2$ salts, even weaker for the $(DCO_2)_2$ salts, and not noticeably shifted by either O- or C-deuteration.

Chemical Structure. The centrosymmetric complexes **1** and **3** both have point group symmetry C_{2h}, and hence the symmetry species and selection rules for their internal vibrations are the same, viz., seven A_g (five within the formate moieties, one O–H–O symmetric stretching, and one moiety vs. moiety in-plane bending); two B_g (out-of-plane bending: one within the formate moieties, one moiety vs. moiety); eight A_u (five within the formate moieties, one moiety vs. moiety in-plane bending, one O–H–O antisymmetric stretching, one O–H–O in-plane bending); four B_u (out-of-plane bending: one within the formate moieties, one O–H–O, two moiety vs. moiety including one torsion).

The six moiety vs. moiety vibrations, including O–H–O symmetric stretching, are expected below 550 cm^{-1}, leaving fifteen above, viz., (five A_g + one B_g) Raman-active and (eight A_u + one B_u) infrared-active fundamentals. Put more concretely, for the centrosymmetric structures one expects one Raman and one infrared band for C–H stretching and likewise for the other vibrations within the formate moieties.

The observed spectra clearly show two infrared bands for at least five of the formate moiety vibrations, and most of them appear also in the Raman spectrum. For $(DCO_2)_2H^-$ and $(DCO_2)_2D^-$ all twelve formate-moiety fundamentals appear in the infrared, and nine of them also in the Raman spectrum. In the solid sodium salt the bis(formate) ion thus does not possess (or nearly possess) C_{2h} symmetry, and structures **1** and **3** are virtually ruled out, though crystal splitting effects have yet to be dealt with.

The above selection rules apply only to the trans forms (and apply *rigorously* only if the O-bound atoms lie on inversion centers in the *crystal*). One now has to consider the other, noncentrosymmetric, structures that are chemically like **1** and **3**, with a symmetrical O--H--O bond and chemically identical formate moieties. For the nonplanar (C_2) and planar cis (C_{2v}) conformations, all vibrations are both infrared (IR) and Raman (R) allowed. The complex still has two composite vibrations (one in-phase and one out-of-phase) for each formate-moiety vibration. If the HCO_2/HCO_2 interplanar angle is near 90°, the separation between in-phase and out-of-phase vibration frequency should be very small. For a planar C_{2v} form, the separations could be appreciable (like the g-u separations for a C_{2h} form).

However, the separations actually observed, such as 120 cm^{-1} between the two CH stretching frequencies, look far too large to be reasonably attributable to any such intramolecular vibrational coupling. That vibrational coupling is *not* the reason why two IR bands are observed (rather than only one), for CH stretching and other vibrations, is shown by the IR spectrum of the isotopic mixture formed from 1:1 $HCO_2H{\cdot}DCO_2Na$ (Figure 1d).

If the complex ions are chemically of the type of **1** and **3**, there are *three* isotopic species in this mixture: $(HCO_2)_2H^-$ (ca. 25%), $(DCO_2)_2H^-$ (ca. 25%), and $(HCO_2)(DCO_2)H^-$ (ca. 50%). With ions of the type of **2** and **4**, there must be four: $HCO_2^-{\cdot}HCO_2H$, $DCO_2^-{\cdot}DCO_2H$, $HCO_2^-{\cdot}DCO_2H$, and $DCO_2^-{\cdot}HCO_2H$ (ca. 25% of each).

The isotopically mixed species $(HCO_2)(DCO_2)H^-$ with two chemically equivalent formate moieties would show *new* bands, one CH stretching band (and *only* one) in place of the two CH stretching frequencies of $(HCO_2)_2H^-$ and about midway between them. Similarly for C–D stretching, in short, the isotopic mixture would show three bands where the isotopically pure species show only two, exactly as was found for solid HCl-DCl mixtures by Hornig and Hiebert.[16] Matters are more complicated for some of the other vibrations, which are still coupled in such an isotopically mixed complex, but, for example, the band that appears at 1366 cm^{-1} for $(HCO_2)_2H^-$ and 1341 cm^{-1} for $(DCO_2)_2H^-$ would appear at ca. 1350 cm^{-1} for this $(HCO_2)(DCO_2)H^-$ ion.

Actually, spectrum 1d shows all the bands present in spectra 1b [$(HCO_2)_2H^-$] and 1c [$(DCO_2)_2H^-$] and *no* extra bands. There is no mixed species $(HCO_2)(DCO_2)H^-$ in which the formate moieties are chemically identical. The chemical nature of the complex is as in structures **2** and **4**, and not as in structures **1** and **3**.

The isotopic mixing technique similarly rules out *intermolecular* coupling as the reason why solid sodium bis(formate) shows almost twice the number of mid-infrared and Raman bands predicted by C_{2h} selection rules. It could be argued that the complex ions may have structure **1** or **3**, but vibrational interaction between crystallographically inequivalent complexes splits each frequency into two. Again, in the isotopic mixture, whenever an HCO_2 moiety has a DCO_2 moiety as its nearest (intermolecular) neighbor, the two frequencies would be replaced by one, about midway between, as in solid HCl–DCl mixtures.[16,17]

An independent piece of evidence, which, however, relates only to the symmetry of the OHO bond, comes from the ratio $\nu(OH)/\nu(OD)$ for hydroxyl stretching. For antisymmetric O--H--O stretching (i.e., if there is a symmetric single-minimum potential) this ratio would be no greater than ca. 0.72 (for the simple harmonic linear triatomic OHO vibrator, it is 0.718); it could be even lower if the quartic anharmonicity term is negative and appreciable.[3,18-22]

The observed ratio is ca. 1.0, a remarkable value, which is possible only if the potential energy curve or hypersurface is highly unsymmetrical around of the equilibrium configuration,[5,23] i.e., if the hydrogen bond is of the type O–H···O as in structures **2** and **4**. (Alternatively, there would have to be a major structural difference between OH and OD complexes; all the spectral evidence indicates that this is not the case here.)

Reference may be made to some well studied type A salts for which there is noncrystallographic, as well as crystallographic, evidence for the presence of a symmetrical O--H--O bond: KH-

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[17] If both inter- *and* intramolecular vibrational couplings give rise to major band splittings and the anion is still assumed to have structure **1** or **3**, the pattern of new bands to be expected for the isotopic mixture is more complicated, but in that case even the "homonuclear" species would show more complicated spectra than observed. Again conditions for observing the complications are favorable in the CH and CD stretching regions.

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$(CF_3CO_2)_2$,[18-20] $NaH(MeCO_2)_2$ (Me = CH_3 or CD_3),[19,21] $KH(CCl_3CO_2)_2$,[21] $RbH(CCl_3CO_2)_2$.[21] All these do show the required low value of $\nu(OD)/\nu(OH)$, quite unlike sodium hydrogen bis(formate). However, like the above four hemisalts, $NaH(HCO_2)_2$ does not show hydroxylic IR bands near 2500 and 1900 cm^{-1}, and in this regard it has a "Hadži–Orel type A"[3] spectrum; in "Hadži–Orel pseudo-type A" spectra, associated with not completely symmetrical OHO systems,[3] these two (separate) bands are present. Crystallographically $NaH(HCO_2)_2$ could well turn out to be a type A hemisalt. (Evidence for hydrogen disorder in a type A salt is very hard to see in diffraction data;[12] an instance of this has been reported, however.[24])

Frequency Assignments. On the basis of an unsymmetrical bis(formate) ion structure as in **2** and **4** most of the assignments are simple; most bands are readily attributed either to complexed formic acid or to complexed formate ion, as in Table I. (The nomenclature for the formate ion vibrations is as in the author's previous work.[25a])

The absence in the spectrum of the isotopic mixture (Figure 1d) of extra bands attributable to the heteronuclear complexes $HCO_2^-{\cdot}DCO_2H$ and $DCO_2^-{\cdot}HCO_2H$ is readily explained: The absorbing entities are complexed formic acid and complexed formate ion. The isotopic composition of the ionic partner (HCO_2^- or DCO_2^-) has no noticeable effect on the absorption of the complexed formic acid; likewise the absorption of complexed formate ion is practically the same whether it is partnered by HCO_2H or DCO_2H (i.e., vibrational coupling across the hydrogen bond does not cause major frequency shifts[26]).

In fact the spectrum of the complexed formate ion here closely resembles that in ordinary metal formates (these have been studied extensively,[25] especially HCO_2Na[25a,28]). All HCO_2^- and DCO_2^- bands are unmistakably recognized in the sodium bis(formate) spectrum, within, or nearly within, their normal frequency range and with their usual relative intensities. Though $\nu_{CO_{st\,I}}$ is almost 20 cm^{-1} higher than for ordinary HCO_2Na, the appearance and relative prominence of the combination and overtone bands above 2000 cm^{-1} provide convincing evidence that the HCO_2^- and DCO_2^- entities, though complexed, are essentially unmodified chemically in solid sodium hydrogen bis(formate).

The formic acid entities, however, *are* modified to a major extent by the very powerful hydrogen bonding. Some of the assignments of the vibrations of HCO_2H, DCO_2H, etc. within the bis(formate) complexes are straightforward only when this has been allowed for. The direct and indirect consequences of strong hydrogen bonding can be deduced by a comparison of the comprehensive IR data for formic acid in (i) the vapor and low-temperature matrix isolation states,[29] (ii) the solid state,[30] in which the molecules are linked into (almost) infinite chains by quite short[31] O—H···O═C hydrogen bonds with $r(O{\cdots}O)$ = 2.58 Å; and (iii) the liquid-phase data for $(HCO_2H)_2$, $(DCO_2H)_2$, $(HCO_2D)_2$, and $(DCO_2D)_2$, given in the Supplementary Material.

The lowering of the O–H stretching frequency on formation of a strong hydrogen bond is accompanied[2b] by a raising of the OH in- (ip bend) and out-of-plane (op bend) bending frequencies; e.g., OH ip bend has been placed at ca. 1500 cm^{-1} for LiO_2CCO_2H (OD ip bend at ca. 1100 cm^{-1})[32] and at 1540 cm^{-1} for $NaH(CH_3CO_2)_2$.[21] For sodium bis(formate) the only one of these bending vibrations that can actually be picked out is OD op bend (near 690 cm^{-1}); OD ip bend and OH op bend fall on top of the IR absorption plateau, OH ip bend presumably is on the slope leading to the plateau, and all are obviously broadened by interaction with OD or OH stretching (presumably Coriolis[33] interaction).

OH ip bend is estimated to be close to 1600 cm^{-1} and OD ip bend around 1150–1200 cm^{-1}, i.e., at much higher frequencies than even in solid formic acid. This has a striking effect on the O-deuteration shifts of three frequencies in the formic acid portions of the complexes: (i) Because $\nu_{OD_{ip\,bend}}$ is so high, it no longer interacts significantly with OCO scissoring; hence $\nu_{OCO_{scis}}$ is not depressed by O-deuteration (whereas it is depressed by ca. 45 cm^{-1} for solid and ca. 60 cm^{-1} for liquid formic acid). (ii) Because $\nu_{OH_{ip\,bend}}$ is so high, it strongly raises $\nu_{C=O_{st}}$ of the complexed formic acid, hence on O-deuteration this frequency drops by ca. 40 cm^{-1} (whereas for liquid $(HCO_2H)_2$ and for $(HCO_2H)_1$ in solid solution in frozen neon[29b] the drop is around 3 cm^{-1}). (iii) Because $\nu_{OH_{ip\,bend}}$ is so high, it does not strongly depress $\nu_{C-O_{st}}$; hence in solid sodium bis(formate) this frequency does not show the anomalous upward shift on O-deuteration found for liquid and solid formic acid.

In addition to the above effects on the mixing of vibrations, the strong hydrogen bonding also has intramolecular structural effects;[34] in particular, it raises[35] the intrinsic $\nu_{C-O_{st}}$. In regard to C═O stretching however, it must be remembered that the C═O oxygen is a hydrogen-bond acceptor in $(HCO_2H)_2$ and $(HCO_2H)_\infty$, but *not* in the complex ions **2** and **4**; hence $\nu_{C=O_{st}}$ is much higher in $NaH(HCO_2)_2$ than in $(HCO_2H)_\infty$ (ca. 1620 cm^{-1}).[30b] The lack of a hydrogen bond to O═C may also be the reason for the absence of this frequency from the Raman spectrum in Figure 2. C═O st bands are often weak in the Raman spectrum, but for liquid formic acid this band is intense.

In the frequency range below 300 cm^{-1}, both intramolecular residue vs. residue motions and lattice vibrations occur. Raman spectra of this region were taken (see Supplementary Material) but band assignments would be too speculative and are not attempted. Concerning H···O (hydrogen bond) stretching, see below.

There are few solid-state complications for $NaH(HCO_2)_2$, and most of the Raman frequencies in Table I coincide with the infrared frequencies within the experimental error. The infrared disk spectra are for dilute dispersions of crystallites of size smaller than the wavelength of the light being absorbed (i.e., "small" particles, in a transparent embedding material), while the Raman spectra are for neat solid powders (in effect in the "large-particle" regime), and perfect agreement between the two sets of frequencies is not to be expected. However, the IR–R frequency differences for C–O st, CO st II, and for CO st I of both HCO_2^- and DCO_2^-

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are large enough to indicate the presence of more than one formula unit in the primitive unit cell of $NaH(HCO_2)_2$.

In the 1700–1600-cm^{-1} range the Raman spectra show two weak bands, 28–36 cm^{-1} apart. Their frequencies being unchanged on O-deuteration and lowered by respectively 7 and 14 cm^{-1} on C-deuteration, they are *both* assigned to vibration CO st I (and not to C=O st; in the IR, $\nu_{C=O_{st}}$ is lowered on O-deuteration by ca. 40 cm^{-1}!). The high IR intensity of CO st I shows the dipole moment change during this vibration ($d\mu/dq$) to be large. Consequent high values of the dipole–dipole interaction energies make feasible an unusually large correlation–field splitting between IR (peak) and R frequency. The 28–36-cm^{-1} separation between the two R bands could be due to transverse optic–longitudinal optic splitting; this, too, is liable to be large when $d\mu/dq$ is large.

Conformation of the Complex Anion. The spectral data for sodium bis(formate) in isolation give no indication as to whether the conformation of the complex is of the type of **2** (and **1**) or of the type of **4** (and **3**). For formic acid in its various states, the only known conformation is planar and has[31,34a] C–H and O–H trans to one another as in **3** and **4**, but in solid $KH(HCO_2)_2$ they are cis to one another[11] as in **1** and **2**. A comparison between the IR spectra of $NaH(HCO_2)_2$ and $KH(HCO_2)_2$ is therefore warranted. It suggests that in the Na salt the conformation is as in **4**.

The Na salt has only one major inverted IR band, at 1400 cm^{-1} for $(HCO_2)_2H^-$ and 1001 cm^{-1} for $(DCO_2)_2H^-$ and $(DCO_2)_2D^-$. The K salt, too, shows this inverted band (at 1392 cm^{-1}), but the most conspicuous inverted band, almost reaching base line, is at 735 cm^{-1} for $KH(HCO_2)_2$ and 730 cm^{-1} for $KD(HCO_2)_2$. Hadži and Orel[3] drew attention to it (giving ν as 720 cm^{-1}) but offered no frequency assignments. On the basis of the results now obtained, this frequency is now confidently assigned to OCO scissoring. *Deep*, appreciably broad, inverted bands ("intense" transmission windows) are expected[5b] if the discrete-frequency vibration that interacts with the continuum vibration, O–H stretching, has a large component of O vibration amplitude along the O–H axis. This is obviously the case in **2** (and **1**), but in **4** the angle between the O–H axis and the direction of the O motion during OCO scissoring is at least 30°, perhaps considerably higher. The sodium bis(formate) bands at 730–721 cm^{-1} all point upward (Figure 1). All this is readily rationalized if the complex has the conformation of **2** in the K salt but that of **4** in the Na salt. (There are other major spectral differences between the two salts, but they are not obviously relatable to conformation.)

The spectra do not indicate whether the complex **4** *as a whole* is coplanar in the Na salt (in the K salt the complex **2**, or **1**, is not[11]).

Potential Energy Hypersurface. A discussion of concentrated *aqueous* sodium hydrogen bis(formate)[36] will contain a qualitative Goodeve-type diagram of potential energy vs. $r(O_I–H)$ and $r(H\cdots O_{II})$ (with a 20° angle between r coordinates) for an idealized permanently linear O–H···O system, designed to apply to the OHO portion of a complex **4** or **2** when[36,37] $\nu_{OD} \approx \nu_{OH}$ for hydroxyl stretching. The (empirically known) strong dependence of ν_{OH} on $r(O\cdots O)$ gives rise to highly anharmonic, and nonseparable, O–H and H···O stretching motions, which, in view of their high amplitudes, are expected to be disordered.[36] Short-term averages (e.g., of vibration frequency) now differ from the long-term averages, from time $t = -\infty$ to time $t = +\infty$ that are normally considered in quantum mechanics. If the short duration of the photonic excitation process is taken into account,[36] this leads to a *range* of energies of excitation, i.e., to a genuine absorption continuum (such as must be present if inverted bands, or "antiresonances",[15] are to occur).

It is implicit in the nonseparability that at least when $\nu_{OD} \approx \nu_{OH}$ there should be a broadened, continuum, type of band also for H···O stretching. Accordingly, the one really broad Raman band, around 450 cm^{-1} (barely visible in the infrared, at ca. 465 cm^{-1}) is tentatively assigned to this.[38]

On the specially interesting question "Is there still a symmetrical double minimum[39] in the potential energy hypersurface in solid sodium bis(formate)?", all that can be said is that there is no positive evidence for one, but conditions for observing one are unfavorable. The great breadth of the OH stretching band in effect precludes observation of the splitting of ν_{O-H} that might indicate one.

Interconversion of the complex **4** into its mirror image converts one kind of OCO scissoring into the other, and similarly for the other vibrations, and would be spectrally observable *if rapid enough*. For the complex $(py)_2H^+$ with an unsymmetrical $N^+–H\cdots N$ bond, Wood[40] predicted, but did *not* observe, splitting of the pyridinic frequencies. Likewise none of the HCO_2 bands of $NaH(HCO_2)_2$ shows such a splitting, or untoward breadth, and probably for the same reason (cf. ref 5b): in **4** the dimensions within the two HCO_2 residues are not expected to be identical, and mere proton tunneling does *not* convert **4** into its mirror image; i.e., in multidimensional energy-configuration hyperspace, the distance between the two potential energy minima is greater than the customary two-dimensional graphs of H position coordinate vs. energy suggest, even for isolated **4**. Surrounding ions compound this. In view of the (multidimensionally) great barrier width, interconversion of **4** is not, a priori, expected to be rapid on the vibrational time scale. As regards the observations, both OCO scis bands of $NaH(HCO_2)_2$ are sharp, even though the separation between them is only 38 cm^{-1}.

Thus, if there is interconversion, it must be slow. Whether there is a symmetrical or a more or less highly unsymmetrical double minimum in $NaH(HCO_2)_2$ (or, in effect, a highly unsymmetrical single minimum) remains unsettled.

Experimental Section

Materials. Solid sodium hydrogen bis(formate) was made[13] from equimolar amounts of pure dry sodium formate and anhydrous formic acid (purified by fractional freezing). Anal. Calcd for $C_2H_3O_4Na$: C, 21.1; H, 2.65; O, 56.1; Na, 20.2. Found: C, 21.25; H, 2.83; O, 55.6; Na, 20.0. The starting materials for the deuterated products (all supplied chemically pure by the manufacturer) were HCO_2D, ca. 99 atom % D (Merck, Sharp and Dohme, Montreal), DCO_2H 98 atom % D (Stohler Isotopes, Rutherford, NJ), DCO_2D 98 atom % D, (Merck, Darmstadt), and DCO_2Na 98.4 atom % D (Wilmad, Buena, NJ). Sodium hydrogen bis(formate) is very hygroscopic in a powdered state, deliquescing at humidities around 60%, and was handled in a manipulator box flushed with dried air. Potassium bromide was dried in vacuo at 110 °C, Nujol over sodium wire and Fluorolube (S30, Hooker Chemical Corp., Niagara Falls) over molecular sieves.

Mull spectra were taken, but sodium hydrogen bis(formate) invariably dissociates appreciably[41] on grinding with mulling agent. Good infrared spectra were obtained in pressed KBr disks (a *small* amount of dissociation, indicated by an HCO_2^- band at 2830 cm^{-1} or a DCO_2^- band at 2131 cm^{-1}, is hard to avoid, however, even during disk pressing).

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[37] For $KH(HCO_2)_2$ the present work gave $\nu_{OH_{st}}$ ca. 1400 cm^{-1} in disks and mulls, for $KD(HCO_2)_2$ $\nu_{OD_{st}}$ ca. 1400 cm^{-1} in disks, and ca. 1300 cm^{-1} in mulls (more concentrated than previously[3] used).

[38] This vibration, often[2] referred to as "O···O" stretching, sometimes as OHO symmetric stretching, is often hard to assign with confidence; e.g., for $KH(CF_3CO_2)_2$ it has variously been placed at 130 cm^{-1}[19] and 792 cm^{-1}.[20]

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Spectra. Infrared spectra (including expanded spectra) were taken with a Perkin-Elmer Model 621 dual-grating spectrophotometer fitted with a Frequency Marker Accessory 221-0348 and flushed with dried air. Raman spectra, normally of the neat solid powders in sealed capillary tubes, were measured with a Japan Spectroscopic Co. Model JASCO R300 spectrometer fitted with a Coherent Radiation Model CR4 argon ion laser; spectral slit widths were in the range 2–3 cm^{-1} and power in the sample compartment 160–320 mW. Frequency precision for reasonably narrow bands is within 1 cm^{-1} in the infrared and within 2 cm^{-1} in the Raman spectra.

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Registry No. $NaH(HCO_2)_2$, 24644-55-1; $NaD(HCO_2)_2$, 84050-15-7; $NaH(DCO_2)_2$, 82941-07-9; $NaD(DCO_2)_2$, 84050-16-8; $NaH(HCO_2)(DCO_2)$, 84050-17-9.

Supplementary Material Available: Frequencies of Raman bands of solid sodium hydrogen bis(formate) below 300 cm^{-1} (Table II); vibrational band frequencies of liquid formic acid (4000–500 cm^{-1}) (Table III) (2 pages). Ordering information is given on any current masthead page.

Correlation between Anisotropic Exchange and Structure of Di-μ-hydroxo Bridged Copper(II) Complexes

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Abstract: The EPR spectra of a series of di-μ-hydroxo bridged copper(II) complexes have been recorded at both X- and Q-band frequency. The zero-field-splitting parameters have been found to be large ($D > 1.1$ cm^{-1}) and to be mainly determined by the exchange interactions between one ion in the ground state and the other one in an excited state. Therefore, the analysis of the EPR triplet spectra provides information on additional exchange pathways as compared to that available through magnetic susceptibility measurements. For the series of complexes the zero-field-splitting parameters are expected to depend mainly on the $J_{x^2-y^2\,xy}$ integral. This is found to be ferromagnetic throughout the series, while the integral involving the ground-state orbitals, $J_{x^2-y^2\,x^2-y^2}$, changes sign. The implications of this finding are discussed within current models for exchange interactions.

Introduction

Di-μ-hydroxo bridged copper(II) complexes still represent the most elegant case in which a successful correlation between structural parameters and extent of exchange coupling has been established.[2–4] At least 11 examples of such complexes are available and for 9 of them linear relations between J, the isotropic exchange constant, and either the Cu–O–Cu bond angle, ϕ, or the Cu–Cu distance have been found.[2–4] For the few cases which deviate from such a behavior, rationale explanations have been produced.[5,6]

The singlet–triplet splitting is mainly determined by the exchange interaction between the ground magnetic orbitals,[7] $J_{g,g}$. However, it is not the only interaction which is experimentally available, but an analysis of the EPR spectra may in principle yield also information on the anisotropic exchange and consequently on the interaction, $J_{g,n}$, between the ground magnetic orbital, g, and an excited one, n.[8] Although this has long been known, we are not aware of any systematic attempt to obtain $J_{g,n}$ for series of complexes and to relate its values to the geometric and electronic features of the complexes.

It is the purpose of this paper to report the EPR spectra of a series of di-μ-hydroxo bridged copper(II) complexes, for which $J_{g,g}$ has been found to vary linearly on the Cu–O–Cu angle from ferro- to antiferromagnetic, and to check whether a similar relationship is valid for the $J_{g,n}$ integrals.

Experimental Section

The $[Cu(bpy)OH]_2X$ ($X = SO_4{\cdot}5H_2O$, $(ClO_4)_2$, $(NO_3)_2$, bpy = 2,2′-bipyridine), $[Cu(tmpd)OH]_2(ClO_4)_2$ (tmpd = *N,N,N′,N′*-tetramethyl-*o*-phenylenediamine), $[Cu(teen)OH]_2(ClO_4)_2$ (teen = *N,N,N′,N′*-tetraethylenediamine), and $[Cu(tmen)OH]_2(ClO_4)_2$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine) complexes were prepared as previously reported.[3,9–12]

The EPR spectra at X- (9 GHz) and Q-band (35 GHz) frequencies were recorded with a Varian E-9 spectrometer. Q-band spectra, with magnetic fields larger than 1.40 T, were recorded at the Department of Chemical Engineering, Twente University of Technology, Enschede, The Netherlands.

Results and Discussion

EPR Spectra. The polycrystalline powder spectra of $[Cu(bpy)OH]_2X$ ($X = SO_4{\cdot}5H_2O$, $(ClO_4)_2$, $(NO_3)_2$), $[Cu(tmpd)OH]_2(ClO_4)_2$, $[Cu(teen)OH]_2(ClO_4)_2$, $[Cu(tmen)OH]_2(ClO_4)_2$, at both X- and Q-band frequency were recorded. The polycrystalline powder and single-crystal EPR spectra of $[Cu(bpy)OH]_2SO_4{\cdot}5H_2O$ were previously reported,[13] but only to the limit of 1.40 T. Some representative examples of spectra at Q-band frequency are shown in Figure 1. The three bpy complexes show very similar spectra, with a feature at low fields, 0.1–0.3 T, and two additional ones in the range 1.5–1.9 T. Also the tmpd complex

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