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SPECTRA-STRUCTURE CORRELATIONS IN THE ISOMORPHOUS SERIES OF METAL(II) SACCHARINATES HEXAHYDRATES

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ABSTRACT

The observed infrared frequencies were correlated with the values of the $O_w\ldots O$ distances in manganese and cadmium saccharinate hexahydrate and the derived correlation equation was used to estimate the corresponding distances in the rest of the metal(II) saccharinates monohydrates.

INTRODUCTION

The hexahydrates of the manganese, iron, cobalt, nickel, zinc and cadmium saccharinates form an isomorphous series of compounds, the details about the structure of the manganese one being already published [1] and the work on the structure of the cadmium analogue being nearly completed [2]. The infrared spectra of the individual members of the series have also been studied by us [3]. The purpose of this paper is to attempt spectra-structure correlations, especially having in view the newly acquired knowledge [2].

EXPERIMENTAL

The studied compounds were prepared according to literature methods [4]. The deuterated analogues (with a low deuterium content) were prepared from suitable H_2O/D_2O) mixtures. The infrared spectra were recorded, at room and liquid-nitrogen temperature (RT and LNT) on a Perkin-Elmer Model 580 spectrophotometer. The details about the structure determinations are given elsewhere [1].

RESULTS AND DISCUSSION

The members of the series crystallize in the space group $P2_1/c$ with four formula units in the unit cell. As anticipated, the parameters of the unit cells are very close to each other [1], the unit-cell volumes reflecting satisfactorily the differences in the metal-ion radii. In the asymmetric unit cell there are a single metal and a single saccharinate ion (the bond between them being apparently not purely ionic), as well as three types of water molecules, the latter forming six types of crystallographically non-equivalent hydrogen bonds.

As expected, the infrared spectra of all these compounds are quite similar, the main differences being associated with the regions of water absorption. Such is the case, for example, with the OD stretching region in the spectra of samples which contain isotopically isolated HDO molecules (Fig. 1), the frequency difference being by far the most pronounced for the lowest-lying of the five bands. In fact, in the spectrum of the Cd compound the fifth band is only barely resolved at LNT (Fig. 1) but shows up clearly at higher temperatures.

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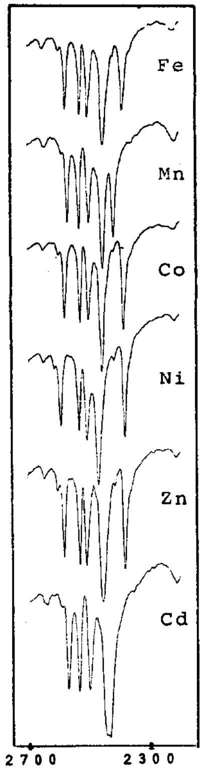

Fig. 1. The OD stretching region in the IR spectra of the studied salts containing isotopically isolated HDO molecules

The existence of *five* bands corresponding to *six* crystallographically non-equivalent protons can easily be explained (as has been done by us even before the structure of the manganese compound was determined [5]), by an accidental coincidence of the structural parameters (distances and angles) around two of the protons. It was rewarding to find out that such was indeed the case for manganese saccharinate hexahydrate [1] where two of the O...O contacts, namely Ow(1)...Ow(3) and Ow(3)...O(3) are in fact equal, each being 281.4 pm long (the remaining Ow...O distances are 274.0, 286.9, 289.6 and 291.5 pm).

In an attempt to correlate the observed O...O distances and OD stretching frequencies, we carried out a regression analysis, using a function of the type

$$R = a\ln\Delta\nu + b$$

where R and $\Delta\nu$ are the numerical values of the O...O distance and of the difference between the OD stretching frequency of gaseous HDO (2727 $\mathrm{cm^{-1}}$) and that observed in the crystal, respectively.

For R measured in picometers and frequencies measured in $\mathrm{cm^{-1}}$, the values of the constants were $a = -24.049$ and $b = 415.6$. The derived correlation equation

$$R = -24.422\ln\Delta\nu + 417.5 \qquad (1)$$

corresponded closely to that which can be obtained by rearranging the published relationship by Berglund et al. [6] to have

$$R = -26.811\ln\Delta\nu + 429.2 \qquad (2)$$

It should be noted, however, that the correlation coefficient was $r = 0.9405$ which is not very high considering the fact that the data come from only two sources - one crystal structure determination and a single spectrum.

Using both Eqn. 1 and 2 as well as the infrared OD frequencies, the O...O distances in the case of the cadmium compound were estimated and are given in Table I together with the experimentally determined ones. As can be seen, the

TABLE I. Predicted and experimental Ow...O distances in cadmium saccharinate hexahydrate

	R/pm					
Predicted (Eqn.1)	278.5	279.4	279.4	284.9	289.0	294.0
Predicted (Eqn.2)	276.6	287.6	287.6	283.6	288.1	293.7
Found [2]	275.3	280.8	281.0	285.9	291.0	291.3

agreement between the predicted and the experimental frequencies is fair, not surprisingly somewhat better when Eqn. 1 was used (this equation, it should be recalled, was obtained from data pertaining to a closely related compound).

When the experimental data for the cadmium compound were included in the regression analysis, Eqn. 3 was obtained

$$R = -23.6091\ln\Delta\nu + 413.1 \qquad (3)$$

and was subsequently used to estimate the Ow...O distances in the remaining four metal saccharinate hexahydrates (the results are summarized in Table II). The correlation curve corresponding to Eqn. 3 is shown in Fig. 2 together with the experimental points for the manganese and cadmium compound.

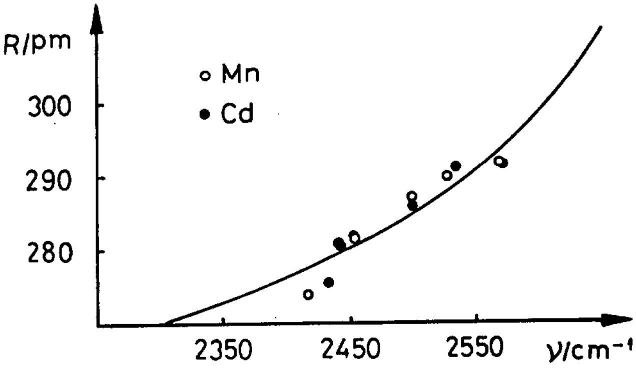

Fig. 2. The *R* vs ν curve derived from Eqn. 3

It should, perhaps, be noted that the scatter of the points around the *R* vs ν curve (Fig. 2) does not depend on the nature of the acceptor oxygens (in the present case they are of three different types and can belong to a carbonyl or an SO_2 group or to another water molecule) to an extent which would be intuitively expected. Thus whereas the largest deviation from this curve is found for the case where the acceptor is one of the carbonyl oxygens (the one taking part in the formation of the strongest hydrogen bond), the second of the two such points lies very close to the curve.

As can be seen in Table II, because of the logarithmic nature of the relationship, the smaller the value of Δν, the larger are the differences in the estimated distances between individual members of the series (compare, for example, columns two and six in Table II: the difference between the smallest and the largest frequency within a column are almost equal - 19 and 21 cm^{-1} respectively, but the difference between the smallest and the largest estimated distance is twice as large in the latter than in the former case). The conclusion which follows is that if one

TABLE II. Observed OD stretching frequencies and estimated Ow...O distances in the hexahydrates of some metal(II) saccharinates

Ni	ν/cm^{-1}	2381	2469	2469	2507	2532	2594
	R/pm	275.1	282.0	282.0	285.8	288.6	297.6
Co	ν/cm^{-1}	2384	2457	2457	2500	2528	2579
	R/pm	275.3	280.9	280.9	285.0	288.1	295.1
Fe	ν/cm^{-1}	2385	2450	2450	2499	2527	2573
	R/pm	275.3	280.3	280.3	284.9	288.0	294.2
Zn	ν/cm^{-1}	2381	2454	2454	2509	2531	2583
	R/pm	275.1	280,8	280.8	286.0	288.5	295.7

is to use correlation equations of the above form, the frequencies of the bands should be measured with precision directly proportional to their value.

Although the prediction of distances from observed frequencies is likely to be the major use of correlation equations such as those introduced by Berglund et al. [6] and discussed here, it is of interest to see how well the OD frequencies can be predicted if the Ow...O distances are known. As a test case we used the distances found in manganese saccharinate hexahydrate [1] and Eqn. 3 (correspondingly rearranged, of course). None of the frequencies is predicted correctly, the differences between the estimated and experimental values ranging from +10 to −51 cm^{-1}, the agreement being the worst for the lowest of the six calculated frequencies.

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