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The Infrared Spectra of Monohydroxamic Acid Complexes of Copper, Iron and Nickel

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A normal coordinate treatment of Cu(MAHA)$_2$, Fe(MAHA)$_2$ and Ni(MAHA)$_2$, (MAHA = N-methylhydroxamic acid) has been carried out, using a 1:1 metal–ligand model and a Urey–Bradley force field. The methyl group was treated as a point mass. Very satisfactory agreements of observed and calculated in-plane infrared frequencies were obtained for copper(II) and iron(III); the metal–oxygen bonds are equivalent, having force constants of ca. *1.08 mdyn/Å. Delocalization does occur over the chelate system resulting in significant double bond character of the C–N bond, and to a lesser extent of the N–O bond.*

Introduction

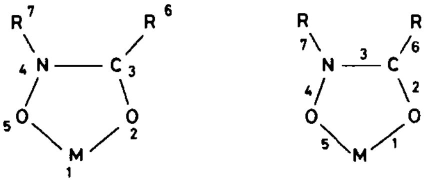
In the previous paper [1], general properties of a variety of hydroxamic acid complexes were discussed. Formerly [2], vibrational assignments have been made on a purely empirical basis. The position of the metal–oxygen and coordinated N–O stretching motions may only be assigned after a normal coordinate analysis, since vibrational coupling is expected to occur in the chelate ring and the concept of 'group frequencies' subsequently breaks down. We carried out a normal coordinate analysis in an attempt to estimate the strength of the M–O bond, to find whether both M–O bonds were equivalent, and to investigate vibrational coupling in the chelate ring for the molecules Cu(MAHA)$_2$, Fe(MAHA)$_3$ and Ni(MAHA)$_2$. Cu(PBHA)$_2$ was also examined to see the effect of altering the methyl group to phenyl (PBHA = N-Phenylbenzohydroxamic acid).

Method

The X-ray analysis of Fe(III) benzohydroxamate trihydrate [3] was used to establish parameters in the following treatment. The systems were treated as planar 1:1 (metal/ligand) complexes. For most of the vibrational modes, the assumption should not cause any serious discrepancy since coupling between ligands should be negligible above 600 cm^{-1}. Any such vibrational coupling should increase as the metal atom becomes lighter and the coordination bond becomes stronger. However, coupling between metal–oxygen bonds belonging to different ligands may be appreciable [4], and the metal–oxygen stretching force constant over-estimated in the 1:1 model.

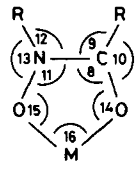
Bands between 4000–1650 cm^{-1} were not included in the calculation as the methyl group was treated as a point mass. Six other bands, present in each of the N-methylacetohydroxamates, at 1435, 1375, 1225, 1028, 652 and 216 cm^{-1} in the case of Cu(MAHA)$_2$, were assigned to methyl asymmetric deformation, methyl symmetric deformation, methyl rocking (in-and-out-of-plane), an out-of-plane bending mode and in a ring out-of-plane mode respectively.

For the Cu(MAHA)$_2$ model, the structural parameters used are given in Table I, and atomic numbering and internal coordination definitions in Figure 1. The 15 normal modes are grouped in 11A$'$ and 4A$''$ vibrations, assuming C$_s$ symmetry. Only the eleven A$'$ (in plane) modes, all of which are infrared active, are considered in the subsequent calculation.



Atom numbering

Bond lengths



Bond Angles

Fig. 1. Atom numbering and internal coordinate definitions for Cu(MAHA)$_2$, 1:1 model.

TABLE I. Structural Parameters for $\mathrm{Cu(MAHA)_2}$, 1:1 Model.

Bond Lengths in Å		
Int. Coord.	Bond	Length Å
1	M–O	1.98
2	C–O	1.28
3	C–N	1.32
4	N–O	1.37
5	O–M	2.06
6	C–R	1.47
7	N–R	1.47
Bond Angles		
Int. Coord.	Bond Angle	Angle°
8	O–C–N	118.2
9	N–C–R	121.1
10	O–C–R	120.7
11	O–N–C	117.2
12	C–N–R	120.7
13	O–N–R	121.1
14	M–O–C	112.6
15	M–O–N	112.6
16	O–M–O	78.7

Seven stretching and nine bending internal coordinates were selected, as shown in Figure 1. A Urey–Bradley field was used, and gem interactions M...C, O...N *etc.* and *cis* contributions R...R and O...O included. The computational procedures of Schachtschneider [5] (CART, GMAT, VBZM, GVIB, FPERT) were utilized. Because of the low symmetry of the system, large matrices of order 16 were necessary; consequently, perturbations involving more than two force constants at a time could not be carried out until there was fairly good initial agreement between observed and calculated frequencies. Table II details observed and calculated frequencies, and their assignment for $\mathrm{Cu(MAHA)_2}$. Table III gives the final stretching, bending and repulsive force constants.

A similar calculation was carried out for $\mathrm{Fe(MAHA)_3}$ and $\mathrm{Ni(MAHA)_2}$ and the results included in Tables II and III. Many attempts were made to carry out similar calculations on the N-phenylbenzohydroxamate complexes using the same geometry as above. However, the use of a point-mass of 77 for the phenyl group, although producing fairly reasonable correlation between observed and calculated frequencies in the case of $\mathrm{Cu(PBHA)_2}$ also gave rise to some rather unrealistic force constants. The calculations did suggest that the metal–oxygen force constants are higher than those of the N-methylacetohydroxamates.

Results and Discussion

In $\mathrm{Cu(MAHA)_2}$ the stretching frequencies of the C–O, C–N and N–O groups were identified on an empirical basis with those bands occurring at 1605, 1465 and 1161 cm^{-1}. The potential energy distribution shows that strong coupling between skeletal vibrational modes takes place. Thus ν_1 (Table II) has 51% C–O and 35% C–N character; ν_2 is 33% C–N, 23% C–R and 17% C–O; ν_3 is 53% N–O and 21% N–R; ν_4 is 33% C–R and 19% N–R and ν_5 is 30% N–R and 17% C–R. Except for ν_8 and ν_9, the A′ vibrational modes below 600 cm^{-1} are coupled in varying degrees to the metal–oxygen stretching modes. ν_6 has 16% O–C–R, 14% Cu–$\mathrm{O_2}$ and 11% O–N–R. ν_8 and ν_9 are ring deformations. ν_{11} is an O–Cu–O bending mode. ν_7 is 22% Cu–$\mathrm{O_5}$ and 13% Cu–$\mathrm{O_2}$, and ν_{10} is 37% Cu–$\mathrm{O_2}$ and 33% M–$\mathrm{O_5}$. Computation of the cartesian displacements for ν_7 and ν_{10} shows clearly that in ν_7 the copper oxygen bonds stretch symmetrically, whilst in ν_{10} they stretch asymmetrically. One would expect, therefore,

TABLE II. Observed and Calculated In-Plane Frequencies for $\mathrm{Cu(MAHA)_2}$, $\mathrm{Fe(MAHA)_3}$ and $\mathrm{Ni(MAHA)_2}$.

	$\mathrm{Cu(MAHA)_2}$		$\mathrm{Fe(MAHA)_3}$		$\mathrm{Ni(MAHA)_2}$	
	$\nu_{\mathrm{obs.}}$	$\nu_{\mathrm{calc.}}$	$\nu_{\mathrm{obs.}}$	$\nu_{\mathrm{calc.}}$	$\nu_{\mathrm{obs.}}$	$\nu_{\mathrm{calc.}}$
ν_1	1605	1609.4	1595	1602.1	1610	1613.5
ν_2	1465	1459.9	1465	1457.3	1485	1439.8
ν_3	1161	1162.8	1168	1169.8	1162	1170.9
ν_4	970	982.7	972	981.3	970	976.7
ν_5	745	734.3	752	738.3	750	738.8
ν_6	600	595.3	600	599.4	600	609.4
ν_7	575	566.3	555	550.1	528	517.0
ν_8	529	511.1	500	502.2	420	448.6
ν_9	358	368.8	358	363.1	382	358.4
ν_{10}	296	287.3	290	278.6	285	290.4
ν_{11}	248	231.7	–	239.0	–	212.9

TABLE III. Stretching, Bending and Repulsive Force Constants for the Metal Hydroxamates Studied.

F. C. Number	Force constant	Value (mdyn/A)		
1	K(M–O_2)	1.15^{a}	1.00^{b}	1.53^{c}
2	K(C–O)	7.51^{a,b}		7.54^{c}
3	K(C–N)	6.47^{a}	6.36^{b}	6.42^{c}
4	K(N–O)	4.50^{a}	4.65^{b}	4.36^{c}
5	K(M–O_5)	1.15^{a}	1.00^{b}	0.74^{c}
6	K(C–R)	3.93^{a,b}		3.60^{c}
7	K(N–R)	2.92^{a,b}		3.60^{c}
8	H(O–C–N)*	0.30		
9	H(N–C–R)*	0.80^{a}	0.70^{b,c}	
10	H(O–C–R)*	0.60^{a}	0.80^{b}	0.90^{c}
11	H(O–N–C)*	0.30		
12	H(C–N–R)*	0.80^{a}	0.70^{b}	0.90^{c}
13	H(O–N–R)*	0.60^{a}	0.51^{b}	0.70^{c}
14	H(M–O–C)*	0.15		
15	H(M–O–N)*	0.15		
16	H(O–M–O)*	0.17^{a}	0.29^{b,c}	
17	F(M....C)	0.05		
18	F(O....N)	0.50		
19	F(C....O)	0.50^{a,b}		0.05^{c}
20	F(N....O)	0.05		
21	F(O....O)	0.05^{a,b}		0.20^{c}
22	F(O_2....R_6)	0.40		
23	F(O_5....R_7)	0.40		
24	F(C....R)	0.40^{a,b}		0.50^{c}
25	F(N....R)	0.50		
26	F(R....R)$^{+}$	0.21		
27	F(O....O)$^{+}$	0.50^{a,b}		0.05^{c}

*Values for the bending force constants have not been corrected for the r^2 factor.

$^{+}$Calculated for the '*Cis*' configuration.

^{a}Cu(MAHA)$_2$. ^{b}Fe(MAHA)$_3$. ^{c}Ni(MAHA)$_2$.

ν_7 and ν_{10} to be considerably separated as given by this treatment. Because of our approximation of a 1:1 ligand–metal model, some care must be taken in the assignment of bands below 400 cm^{-1}. Since vibrational coupling between different chelate rings reduces as the metal–oxygen bands become weaker, in view of the relatively small value of K_{Cu-O}, we would expect a reasonably accurate result in the low frequency region. In fact, the observed and calculated frequencies of all bands in Table I, in the copper case, show good agreement to within 1.98%.

Supporting evidence for our assignment of ν_7 as a copper–oxygen stretching mode comes from a study of structurally analogous substituted salicylaldehyde complexes [6] of Cu(II), Ni(II) and Co(II), which on the basis of metal ion and isotopic substitution placed a metal–oxygen stretching mode between 620–580 cm^{-1}. The band assigned by us as ν_7 in Cu(MAHA)$_2$ is metal sensitive (it occurs at 555 cm^{-1} in Fe(MAHA)$_3$). A spectrum of Cu(PBHA)$_2$, substituted with the ^{63}Cu isotope, showed that bands at 574 and 298 cm^{-1} each showed a blue shift of 3 cm^{-1}. This again gives credence to our assignments of the metal–oxygen frequencies ν_7 and ν_{10} in Cu(MAHA)$_2$.

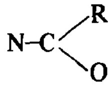
Our C–O stretching force constant of 7.4 mdyn/Å is considerably higher than that found for metal glycolato complexes [9] (6.4 mdyn/Å), metal glycino [10] complexes (6.3 mdyn/Å), metal biuret [11] complexes (6.7 mdyn/Å), and slightly higher than that [12] for Cu(acac)$_2$ (7.2 mdyn/Å) indicating retention of a considerable amount of double bond C–O character. The C–N force constant is also much higher than that of Cu(glycino)$_2$ complexes [10]. On the basis of a diatomic oscillator, an N–O band at 900 cm^{-1} would have a K_{N-O} of 3.56 mdyn/Å; at 1150 cm^{-1}, K_{N-O} of 3.56 mdyn/Å; at 1150 cm^{-1}, K_{N-O} would correspond to 5.81 mdyn/Å. In hydroxylamine [13], the N–O (A′) stretching frequencies have been assigned to a band at 912 cm^{-1}. Our K_{N-O} of 4.50 mdyn/Å for Cu(MAHA)$_2$ indicates some double bond character existing, and shows the effect of vibrational coupling on the N–O stretching frequency, since ν_{NO} in Cu(MAHA)$_2$ occurs at 1161 cm^{-1}.

In the case of Fe(MAHA)$_3$ the spectrum of which correlates almost band for band with Cu(MAHA)$_2$, assignments of frequencies and the potential energy distribution is essentially the same as for Cu(MAHA)$_2$. The principal metal–oxygen frequency at 558 cm^{-1} is lower than for copper, and the second one is split into two components, separated by 18 cm^{-1}. We calculated this lower frequency to fit the mean of the two observed frequencies at 280 and 298 cm^{-1}. In the case of octahedrally coordinated Fe(acac)$_3$, a full [7] NCA (3:1 model) showed it to have three infrared-active metal–oxygen stretching frequencies, the first being a symmetrical stretching motion, and the other two corresponding to the asymmetric case, subject to a small separation with a splitting between symmetric and asymmetric frequencies of a similar order of magnitude as in the monohydroxamic acid complexes.

The spectrum of Ni(MAHA)$_2$ shows significant variation from those previously considered. The bands at 575–558 cm^{-1} are replaced by a band at 592 cm^{-1}, a new band appears at 420 cm^{-1}, and the band at 360 cm^{-1} moves upwards to 382 cm^{-1}. The bands at 420 cm^{-1} and 285 cm^{-1} have been assigned to the ν(Ni–O) modes by comparison with Co(glycolato)$_2$ [8], where they occur at 443 and 316 cm^{-1}. The Ni–O force constants are no longer equivalent. The fact that the nickel complex is an octahedrally coordinated oxygen bridged tetramer obviously introduces severe limitations into the treatment.

The X-ray data [3] for Fe(BHA)$_3$·3H$_2$O gives C–O, C–N and N–O bond distances of 1.30, 1.37 and 1.36 Å respectively. The sum of single-bond covalent radii indicate bond distances of 1.43, 1.47 and 1.36 Å. In hydroxylamine, the N–O bond distance is 1.46 Å. Thus the calculated force constants which indicate substantial double bond character in the C–O and C–N bonds, and to a lesser degree in the N–O bond are consistent with these values.

In the case of (MAHA) complexes, the C–O frequency increases as the M–O frequency increases and the C–N frequency decreases, indicating extensive coupling, as the C–O bond would be expected to decrease as the frequency of the M–O bond increases. The N–O band and stretching force constant increase as the M–O band decreases. The relative constancy in position of C–O, C–N and N–O bands is interesting.

Our results clearly show that the assignment of the N–O stretching mode to a band at *ca.* 930 cm^{-1} in previous investigations [2] is incorrect. These results also confirm that vibrational coupling occurs between the chelate ring vibrational modes, and the subsequent mixing reduces the effect of the central atom change, and also of substitution in the chelate ring. Electron delocalization over the entire ring (*cf.* acetylacetonato [7] complexes) does occur, more particularly in the  $N{-}C\langle^{R}_{O}$ moiety.

The similarity of force constants for Cu and Fe suggests that the strength of both metal–oxygen bonds is similar, *i.e.* both have the same covalent character. This effect has previously been noticed in the case [8] of $Co(glycolato)_2$. Since the metal–oxygen stretching constants are lower than those found for the corresponding acetylacetonates (2.25 mdyn/Å) indicating little d_π–p_π bonding, the calculated force constant values are probably close to the actual since the effects of π-bonding exaggerate the inaccuracies introduced by the 1:1 model. The force constant for Cu–O obtained is similar to that in $Cu(biuret)_2$ (1.17 mdyn/Å) [11], $Cu(glycolato)_2$ (1.0 mdyn/Å) [8] and slightly larger than those for $Cu(glycino)_2$ of 0.9 mdyn/Å [10]. These values are consistent with considerations [1] of the electronic and e.s.r. spectra which show the effect of π-bonding and degree of covalency to be quite small.

Experimental

Infrared spectra were recorded as 2% CsBr discs on Perkin Elmer 337 and 457 instruments. Far infrared spectra were obtained on a Grubb Parsons Cube Interferometer. The observed bands for the hydroxamic acid complexes are:

Cu(MAHA)₂: 3400(b, w), 3245(w), 2984(w), 2930(m), (2909), 1605(s), 1465(s), 1435(s), (1405), (1388), 1379(w), 1225(m), 1200(w), 1161(s), 1028(s), 970(s), 745(s), 652(s), 638(w), 610(m), 575(m), 529(m), 500(w), (380), 358(m), (325), (305), 296(w), 280(w), 248(w), 216(w), (184), (100).

Cu(PBHA)₂: 3410(m, b), (3090), (3060), 3050(s), (3030), (3010), 2929(w), 2851(w), 1585(s), (1569), 1545(s, b), 1491(w), 1460(s), 1445(s), 1312(w), 1290(w), 1165(m), 1071(m), 1036(m), 1013(s), 1000(m), 941(s), 920(m), (772), 767(s), 725(m), (707), 694(s), 674(m), 615(w), 600(w), 574(m), 510(m), (489), 457(m), 442(m, sh), (370), 314(w), 306(w), 298(w), 284(w), 276(w), 253(m), 216(m), 109(m).

Fe(MAHA)₂: 3420(m, b), (3000), 2930(w), 1595(s), 1465(s), (1455), 1428(m), 1380(w), 1229(m), 1168(s), (1118), 1030(m), 972(s), 752(s), 627(s), 600(w), 555(s), 500(w), 358(w), 300(m), 298(m), 280(w).

Ni(MAHA)₂: 3420(m, b), 2930(m), (2831), (2800), (1710), 1610(s), 1485(m), 1430(m), 1409(m), 1366(m), 1221(m), (1200), 1162(s), 1031(m), 970(s), 750(s), 629(s), 600(w), 528(m), 420(m), 382(m), 285(m), 250(w).

Accuracy is believed to be ±2 cm^{-1} over the observed range. Shoulders are given in parenthesis.

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