

ration is relatively small, so that an appreciable proportion of molecules will populate the lowest triplet state; but on increasing the temperature since the energy separation increases more rapidly than  $RT$ , the number of molecules in the triplet state will become smaller. Above a certain temperature  $\Delta E$  remains practically constant, so that the increase of thermal energy causes an increase of the population of the lowest triplet state.

As shown in Tables I and II, the values of  $\Delta E$  at a given temperature are nearly identical for the solutions and the melts. Also the spectra of the melt and of benzene solution, although measured at different temperatures, are found to be very similar. This confirms that fusion, *i.e.*, self-solution, alters the effective ligand field around the nickel ion, in a way very similar to that of dissolution in a solvent.

In the case of the bis-(*N*-methylsalicylaldehyde)-nickel(II) complex the values of the energy separation are lower than in the other complexes, ranging from 1.3 at 20° to 2.9 at 120°. The values of  $\Delta E$  for the same complex, calculated using Clark's data for magnetic measurements in  $\text{CHCl}_3$  and toluene,<sup>2</sup> are even lower, becoming negative at temperature below -10°. Under these conditions, therefore, the triplet state is the most stable.

Another peculiar feature of the methyl complex is the fact that, on heating above 150°, it transforms into a paramagnetic solid isomer with  $\mu_{\text{eff}} = 3.4$  B.M.<sup>8</sup> This has been attributed to the attainment of a six-coordinated structure, through the formation of intermolecular bonds along the *z*-axis, between nickel and donor atoms of two adjacent

molecules of the complex. The crystal field acting on the nickel atom would in this case approach a distorted octahedron, and the ground state would be paramagnetic.

A similar explanation implying an equilibrium between diamagnetic planar monomers and octahedral paramagnetic polymers could also be postulated for the temperature dependent paramagnetism in the melts. Such a suggestion, however, does not agree with the results of the viscosity measurements. In fact in our measurements of the viscosity of the octyl- and nonyl-complexes we found a practically linear relationship between  $\ln \eta$  and  $1/T$  over a wide range of temperature (Fig. 2). As is well known this behavior is peculiar to unassociated liquids.

This conclusion does not contradict the above assumption that the molecular interactions decrease as the temperature increases. In fact, a comparison of the values of  $\mu$  and  $\Delta E$ , for the melts and for the corresponding solutions in solvents such as benzene and dibutyl phthalate, shows that they are almost equal and quite different from those of the solutions in pyridine. The molecular interactions responsible for the axial perturbation of the field acting on the nickel ion in the melts must therefore be weak and almost equal to those established between the molecules of the complex and of the inert solvents. Thus it is not surprising that the variation of viscosity with the temperature is "normal."

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[CONTRIBUTION FROM THE McPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

## The Infrared Spectra of the Complexes of Iron(II), Cobalt(II) and Nickel(II) with Biacetyldihydrazone

By R. CARL STOUFER<sup>1a</sup> AND DARYLE H. BUSCH

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The infrared spectra of the complexes of iron(II), cobalt(II) and nickel(II) with biacetyldihydrazone (BdH) have been determined. Assignments have been made in the case of twelve different absorptions. The position of the C=N stretching frequency of BdH is sensitive to the type of complex which is formed. The data, which are presented herein, are consistent with the formation of multiple bonds (both sigma- and pi-bonds) in the diamagnetic complex, tris-(biacetyldihydrazone)-iron(II) iodide. The spectra of the paramagnetic cobalt(II) and nickel(II) complexes indicate that the interaction between the metal atom and the imine nitrogen atom of the ligand molecule is not as great as that which exists in the diamagnetic iron(II) complex. The conformation of biacetyldihydrazone is discussed.

### Introduction

It has been demonstrated that the complexes which biacetyldihydrazone forms with iron(II), cobalt(II) and nickel(II) are very similar to the complexes which these dipositive metal ions form with ligand molecules of the dipyridyl type, *e.g.*, 2,2'-bipyridine and *o*-phenanthroline.<sup>1b</sup> Tris-(biacetyldihydrazone)-iron(II) iodide is diamagnetic whereas the corresponding three-to-one cobalt(II) and nickel(II) complexes are paramagnetic. The two-to-one complexes of cobalt(II) and nickel(II), *viz.*,  $[\text{Co}(\text{BdH})_2\text{Cl}_2]$  and  $[\text{Ni}(\text{BdH})_2\text{Cl}_2]$ , are also

highly paramagnetic, indicating three and two unpaired electrons, respectively.

Of the complexes formed by these metal ions with aromatic heterocyclic diamines, acyclic diimines and dihydrazones, only the iron(II) complexes are consistently highly colored. It has been suggested by other investigators that the properties of these iron(II) complexes which distinguish them from those of cobalt and nickel are a consequence of pi-bonding between the conjugated ligand molecules (all of which contain the conjugated dimethine group) and the  $t_{2g}$  (non-bonding) electrons of the iron atom.<sup>2,3</sup>

(1) (a) University of Florida, Gainesville. (b) R. C. Stoufer and D. H. Busch, *THIS JOURNAL*, **78**, 6016 (1956).

(2) P. Krumholz, *ibid.*, **76**, 2163 (1953).

(3) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 1137 (1956).

TABLE I

INFRARED ABSORPTION BANDS (CM.<sup>-1</sup>) FOR BIACETYLDIHYDRAZONE (BdH) AND ITS COMPLEXES

The abbreviations used in the first column of the table of assignments<sup>7</sup> are: st, bond stretching vibration; d, deformation vibration; r, rocking vibration; -s, symmetric vibration; -a, asymmetric vibration; ?, assignment uncertain. The abbreviations used in the body of the table of assignments to indicate the relative intensities of the absorptions<sup>7</sup> are: vs, very strong; s, strong; m, medium strong; w, weak; vw, very weak. The symbols in parentheses used to describe the nature of the absorption<sup>7</sup> are: (b), broad absorption; (d), partly resolved doublet (average value); (d1), short frequency member of a resolved doublet; (d2), long frequency member of a resolved doublet; (nr), not resolved; (sh), shoulder on a band of higher intensity; (d), unresolved doublet, frequency given is average. <sup>b</sup> Liquid sample. <sup>c</sup> Deuterated sample.

Assignment	Biac <sup>b</sup>	BdH	BdH <sup>c</sup>	[Fe(BdH) <sub>3</sub> ] <sub>2</sub>	[Fe-(BdH) <sub>3</sub> ] <sub>2</sub> <sup>c</sup>	[Co-(BdH) <sub>2</sub> Cl <sub>2</sub> ]	[Co-(BdH) <sub>2</sub> Cl <sub>2</sub> ]	[Ni-(BdH) <sub>2</sub> Cl <sub>2</sub> ]	[Ni-(BdH) <sub>2</sub> Cl <sub>2</sub> ]
H <sub>2</sub> O	..	3484m	3460m	3413s	3356s	3390s	3401s	3401s	3378s
st-a NH <sub>2</sub>	..	3367 vs	..	3289vs	..	3279s	3311s	3268s	3279s
st-s NH <sub>2</sub>	..	3215vs	..	3185vs	..	3215s	3215s	3226s	3165s
st-a ND <sub>2</sub>	..	..	2500s	..	2513s	..	..	..	..
st-s ND <sub>2</sub>	..	..	2342s	..	2342w	..	..	..	..
st CH	2994w 2933w	3040w 2959m	3012w 2950m	2907vw ..	2924vw ..	2907w ..	2907w ..	2941w ..	2933(sh) ..
st C=D	1724vs 1681(sh)	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..
d NH <sub>2</sub>	..	1645m	..	1621(sh)	..	1633(sh)	1637s	1634s	1639(sh)
d ND <sub>2</sub>	..	..	1221m	..	1225m	..	..	..	..
st C=N	..	1582m	1577s	1595s	1595s	1623s	1613s	1613s	1613s
d-a C-CH <sub>3</sub>	1422m	1464m	1456m	1445m	1439m	1441w	1451m	1449m	1441m
	..	1441m	1437m	..	..	..	..	..	..
d-s C-CH <sub>3</sub>	1353s	1370s	1348s	1374m	1372m	1383m	1364m	1383m	1376m
d,r NH <sub>2</sub>	..	741s(b)	..	749m(b)	..	790vw	726w(b)	739vw	777w(b)
	..	664w	..	682m	..	763vw	682w	685vw	682w
	..	..	..	..	..	682vw	..	..	..

Metal ion-ligand pi-bonding may be of two general types. The central metal atom may possess paired electrons which are shared with ligand molecules through available *p* orbitals or *d* orbitals on the ligand<sup>4</sup> or the ligand molecules may have pairs of electrons in *p* orbitals which are not used in sigma-bond formation and which are of the proper symmetry to overlap unfilled *t<sub>2g</sub>* orbitals of the metal atom.<sup>5,6</sup> A *d<sup>6</sup>* ion, such as iron(II), would be expected to form pi-bonds of the first types since the *t<sub>2g</sub>* orbitals are filled. Orgel<sup>6</sup> pointed out that, on the basis of crystal field theory, spin-pairing is not expected of iron(II) in complexes with the ligands of the dipyriddy type (specifically, *o*-phenanthroline). The fact that these complexes are low-spin is interpreted as an indication that pi-bonding is an important factor.

The purpose of this study is to correlate the change in infrared spectral properties of these compounds with the apparent change in bond type between metal and ligand molecule. Particular attention will be given to the double bond region of the spectra (1750-1400 cm.<sup>-1</sup>). Differences in the interaction between the metal atoms and ligand molecules should be reflected by changes in the position or intensity of the acyclic C=N stretching frequency. Such effects have been considered<sup>3</sup> in systems involving iron(II) and the conjugated dimethine group; however, the present system lends itself, more easily, to interpretation due to the simpler structure of the ligand molecule.

(4) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 227-231.

(5) L. E. Orgel and J. S. Griffith, *Quart. Revs. (London)*, **11**, 381 (1957).

(6) L. E. Orgel, "Some Applications of Crystal-field Theory to Problems in Transition-Metal Chemistry," *Report to the Xth Solvay Council, Brussels, May, 1956*.

## Experimental

The methods of preparation for the compounds which were used to determine the spectra listed herein were reported previously.<sup>1b</sup>

The infrared spectra were obtained by using a Model 21 Perkin-Elmer Infrared Recording Spectrophotometer equipped with sodium chloride optics. The potassium bromide pellet method was used for solid samples and sodium chloride capillary cells for the liquid sample (2,3-butanedione).

Deuteration of selected samples was accomplished by dissolving approximately 30 mg. of the sample in the minimum amount of deuterium oxide. The deuterium oxide was subsequently removed by distillation at reduced pressure and the samples were dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

## Results

The assignments proposed for twelve absorptions which appear in the spectra of seven different compounds are in accord with the usual frequency ranges reported for the groups in question<sup>7,8</sup> (Table I).

In the spectra determined by the KBr disk method, a band attributable to water occurs in the 3500 cm.<sup>-1</sup> region (Table I). This absorption will not be considered further.

**2,3-Butanedione.**—The absorptions of biacetyl, which are listed in Table I, are in agreement with those reported previously.<sup>9</sup>

**Biacetyldihydrazone (BdH).**—The two strong bands of approximately equal intensity, which occur at 3367 and 3215 cm.<sup>-1</sup>, are attributed to the antisymmetric and symmetric NH<sub>2</sub> stretching vibrations. The positions of these bands are some-

(7) H. M. Randall, R. G. Fowler, J. Fuson and J. R. Dangel, "Infrared Determinations of Organic Structures," D. Van Nostrand Company, Inc., New York, N. Y., 1949.

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(9) Ref. 7, p. 167, Table V.

what lower than those usually associated with these vibrations (3500 to 3300  $\text{cm}^{-1}$ ). This may be the result of interaction between the nitrogen atom of the  $\text{NH}_2$  group and the imine nitrogen atom, both of which have electron pairs with pi symmetry. Alternatively, the positions of these bands may be associated with the fact that this spectrum was obtained by using a solid sample. Upon deuteration, two new bands appear at 2500 and 2342  $\text{cm}^{-1}$ . These bands are similar in shape and relative intensity to the  $\text{NH}_2$  stretching vibrations in the spectrum of the undeuterated sample and are assigned to the two  $\text{ND}_2$  stretching vibrations.

Two absorptions of similar intensity occur at 1645 and 1582  $\text{cm}^{-1}$  (Table I). Deuteration of the sample results in the virtual elimination of the 1645  $\text{cm}^{-1}$  band while the 1582  $\text{cm}^{-1}$  absorption is unchanged; therefore, the 1645  $\text{cm}^{-1}$  absorption is assigned to the  $\text{NH}_2$  internal deformation mode while the 1582  $\text{cm}^{-1}$  band is assigned to the  $\text{C}=\text{N}$  stretching vibration.

The antisymmetric and symmetric  $\text{C}-\text{CH}_3$  deformation vibrations lie at 1464–1441 and 1370  $\text{cm}^{-1}$ , respectively. These absorptions are very similar to those of biacetyl, the symmetrical deformation frequency giving rise to a much stronger band than the antisymmetric mode. There is the difference, however, that the antisymmetric mode is doubled in the spectrum of biacetyldihydrazone. This is an occurrence not uncommon in the solid state.<sup>10</sup> This antisymmetric  $\text{C}-\text{CH}_3$  deformation doublet is well resolved into two bands which have maxima lying at 1464 and 1441  $\text{cm}^{-1}$ . The splitting of this band is also observed in the spectrum of the deuterated sample of biacetyldihydrazone.

The strong, broad absorptions which occur at 741 and 664  $\text{cm}^{-1}$  are assigned to the external deformations (rocking vibrations) of the  $\text{NH}_2$  groups.<sup>11,12</sup> These absorptions are absent in the spectrum of the deuterated sample.

**Complexes of Biacetyldihydrazone.**—A number of regular changes are apparent upon comparing the spectrum of biacetyldihydrazone with the spectra of the complexes of this ligand. The absorptions of these complexes which are attributed to the  $\text{NH}_2$  antisymmetric stretching frequency appear at a position somewhat lower than in the spectrum of the free ligand. They occur in the range 3268–3311  $\text{cm}^{-1}$  (Table I). In addition, these absorptions are somewhat less intense, in the spectra of the complexes, than the symmetrical stretching mode. As stated above, these two stretching frequencies are approximately equal in intensity in the spectrum of the free ligand. On the other hand, the positions of the symmetrical  $\text{NH}_2$  stretching vibrations lie very close to that found in the spectrum of the free ligand (3215  $\text{cm}^{-1}$ ). Also, in the spectrum of any given complex, the relative intensity of this band, with respect to the other bands in the spectrum, is quite similar to the corresponding relationship observed in the spectrum of the uncoordinated ligand. It should be pointed out, however, that no great

significance should be attached to the observed change in position of the  $\text{NH}_2$  stretching vibrations because of the low dispersion of sodium chloride optics in this region.

The  $\text{NH}_2$  deformation vibrations of these complexes are shifted to slightly lower frequencies, the shift being most marked in the case of  $[\text{Fe}(\text{BdH})_3]\text{I}_2$  (24  $\text{cm}^{-1}$ ). This corresponds to approximately twice the shift observed for the cobalt(II) and nickel(II) complexes (Table I). Assignment of this band in the spectra of the two-to-one cobalt and nickel complexes is rendered somewhat difficult because it appears merely as a shoulder on the stronger  $\text{C}=\text{N}$  absorption. Furthermore, these two complexes cannot be deuterated by dissolving them in  $\text{D}_2\text{O}$  because the three-to-one complexes are formed.<sup>1b</sup>

Significant shifts are apparent for the  $\text{C}=\text{N}$  stretching frequency throughout the series of five metal complexes. Whereas this band is at 1582  $\text{cm}^{-1}$  in the spectrum of the free ligand, it occurs at increasingly higher frequencies for the complexes in the following order:  $[\text{Fe}(\text{BdH})_3]\text{I}_2 < [\text{Ni}(\text{BdH})_2\text{Cl}_2] = [\text{Ni}(\text{BdH})_3]\text{Cl}_2 = [\text{Co}(\text{BdH})_3]\text{I}_2 < [\text{Co}(\text{BdH})_2\text{Cl}_2]$ . The difference in the position of this band in the two-to-one cobalt complex and that in the spectrum of the free ligand is 41  $\text{cm}^{-1}$ .

The positions of the  $\text{C}-\text{CH}_3$  deformation vibrations experience a rather irregular shift from spectrum to spectrum; however, a regular alteration in relative intensities is observed (Table I). Whereas the symmetrical deformation is more intense than the antisymmetric deformation in the spectrum of the free ligand and of biacetyl, the intensity of the symmetrical mode is reduced, in the spectra of the complexes, to an intensity only slightly greater than that of the antisymmetric deformation. The latter remains relatively unchanged in intensity.

The  $\text{NH}_2$  external deformation vibration which occurs near 741  $\text{cm}^{-1}$  in the spectrum of the free ligand experiences an irregular shift among the spectra of the complexes, while the second absorption at 664  $\text{cm}^{-1}$  is shifted to approximately 682  $\text{cm}^{-1}$  in the spectra of the complexes (remaining unchanged from spectrum to spectrum).

### Discussion

Two points should be emphasized with respect to the spectrum of biacetyl. The position and character of the carbonyl absorption, when considered in conjunction with Raman spectra data, indicate that the interaction between the two "conjugated"  $\text{C}=\text{O}$  bonds is very small.<sup>13,14</sup> Furthermore, electron diffraction data indicate that the molecule exists in a *trans* conformation.<sup>15</sup> LuValle and Schomaker have calculated that the *trans* conformation of biacetyl is 1.7 kcal./mole more stable than the *cis* conformation.

Considering the evidence for the existence of biacetyl in the *trans* planar conformation, it is not unreasonable to expect a *trans* planar conformation for the corresponding hydrazone. Certainly such

(13) Ref. 7, pp. 17, 18.

(14) Ref. 8, p. 122.

(15) J. E. LuValle and V. Schomaker, *THIS JOURNAL*, **62**, 988 (1940).

(10) Ref. 8, p. 21.

(11) Ref. 8, pp. 218–219.

(12) Ref. 7, Table V and p. 61.

a conformation would constitute the state of lowest electrostatic repulsion between two relatively negative  $\text{NH}_2$  groups, and it may also be seen, in a qualitative manner, from the representations of both the *cis* and *trans* planar conformations (Fig. 1) that steric hindrance would be greater in the *cis* conformation than in the *trans* conformation. This steric hindrance (which arises from the several repulsions between the two methyl groups and the two amine groups) would tend to distort the planarity of the molecule thus reducing the effective interaction of the pi electrons of the system.

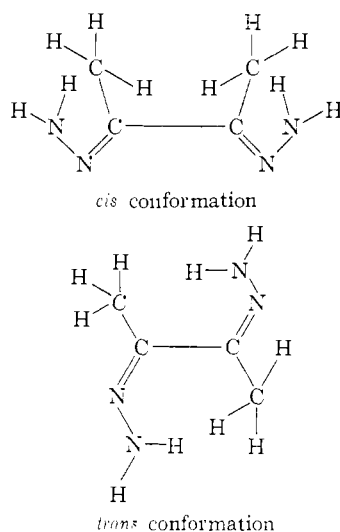


Fig. 1.

It should be recalled at this point that the  $\text{NH}_2$  internal deformation mode and the  $\text{C}=\text{N}$  stretching mode of biacetyldihydrazone occur at 1645 and 1582  $\text{cm}^{-1}$ , respectively. However, on the basis of the usual positions of these two bands, one would expect the  $\text{C}=\text{N}$  stretching vibration to be associated with the higher of the two bands.<sup>16</sup>

Electronically the dimethine portion of biacetyldihydrazone is analogous to butadiene. The pi-electron interaction expected for such a structure would serve to lower the  $\text{C}=\text{N}$  stretching frequency with respect to that of a single, isolated  $\text{C}=\text{N}$  bond. It has been indicated from other investigations that the lowering in frequency is proportional to the degree of conjugation.<sup>17</sup>

Interaction between the amine nitrogen atom and the imine nitrogen atom to which it is bonded also appear to be of significance. In order for the  $\text{NH}_2$  group to exhibit a conjugative effect, the structure of the group would have to be distorted toward the limiting trigonal planar array of sigma-bonds (about the nitrogen atom) in order to bring the unshared electron pair of the  $\text{NH}_2$  group into pi symmetry with the pi electron system of the remainder of the molecule. It can be seen from Table I that the  $\text{NH}_2$  stretching modes of these compounds occur at lower frequencies than is commonly observed. This is in agreement with a decrease in electron density on the amine nitrogen atom. Two other observations support this sug-

(16) Ref. 8.

(17) R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1382 (1958).

gested conjugative effect. The  $\text{C}=\text{N}$  stretching frequency is found at higher values in the spectra of molecules such as benzaldazine and pyridinaldazine (1634 and 1620  $\text{cm}^{-1}$ , respectively)<sup>18</sup> in which conjugation of two adjacent  $\text{C}=\text{N}$  groups occurs but is not complicated by the presence of an  $\text{NH}_2$  group. Also, only a single  $\text{C}=\text{N}$  stretching vibration is observed in the spectrum of BdH, not two which would be expected from a *cis* conformation and a significant interaction between the two  $\text{C}=\text{N}$  groups in "conjugated" position. The interaction which is suggested is represented, diagrammatically, in Fig. 2.

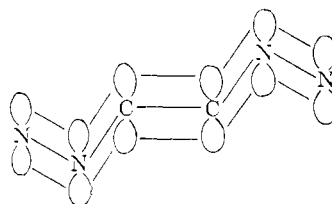


Fig. 2.

The observation which was made previously, pertaining to the location of the  $\text{C}=\text{N}$  stretching vibration in the spectra of the complexes, *viz.*, upon complex formation, the  $\text{C}=\text{N}$  stretching vibration occurs at increasingly higher frequencies for the complexes in the order  $[\text{Fe}(\text{BdH})_3]\text{I}_2 < [\text{Ni}(\text{BdH})_2\text{Cl}_2] = [\text{Ni}(\text{BdH})_3]\text{I}_2 = [\text{Co}(\text{BdH})_3]\text{I}_2 < [\text{Co}(\text{BdH})_2\text{Cl}_2]$ , may be accounted for on the basis of decreasing interaction between the metal atom and ligand groups. The iron(II) complex, which is clearly of the robust type, being diamagnetic and resolvable into optical isomers,<sup>19</sup> is most likely to involve metal-ligand pi-bonding of the type discussed previously. This complex has the lowest  $\text{C}=\text{N}$  stretching frequency of any of the complexes (1595  $\text{cm}^{-1}$ ). On the other hand, the properties of  $[\text{Co}(\text{BdH})_2\text{Cl}_2]$ , which indicate that this complex is relatively weak (and in which case it is assumed that metal-ligand pi-bonding is unimportant), has the highest  $\text{C}=\text{N}$  stretching frequency (1623  $\text{cm}^{-1}$ ).

The remaining complexes exhibit an intermediate behavior and it is inferred that metal-ligand pi-bonding is relatively unimportant, although its presence is apparent. Thus it is seen that these experimental data are in agreement with the trend which one would predict on the basis of other physical and chemical properties of these complexes.

Upon considering, further, the arguments which were invoked to account for the relative positions of the  $\text{C}=\text{N}$  stretching frequencies in the spectra of the complexes, one would expect the  $\text{C}=\text{N}$  absorption to occur at lower frequencies in the spectra of the complexes (in which multiple bonding is present) than in the spectrum of the free ligand. The opposite is true (compare 1582  $\text{cm}^{-1}$  in the spectrum of biacetyldihydrazone with 1595  $\text{cm}^{-1}$  in the spectrum of  $[\text{Fe}(\text{BdH})_3]\text{I}_2$ ). This seeming anomaly may be explained in terms of the interactions occurring in the biacetyldihydrazone molecule, as discussed earlier. In so doing it is conven-

(18) W. J. Stratton and D. H. Busch, Paper presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

(19) R. C. Stoufer, Thesis, Ohio State University, 1959.

ient to first account for shifts occurring in cases involving relatively little pi-bond formation, e.g.,  $[\text{Co}(\text{BdH})_2\text{Cl}_2]$ .

It was suggested that a large contributing factor to the low position of the C=N band in biacetyldihydrazone is associated with the *trans* planar conformation of the molecule, which would facilitate conjugation of the  $\text{NH}_2$  group and the two C=N groups. However, upon formation of a chelate ring, the ligand is required to assume a *cis* conformation. Consideration of a physical model suggested that, in the case of a *cis* conformation, not only do the two adjacent methyl groups interfere with each other, but the  $\text{NH}_2$  groups press back upon the molecule. These two factors then suggest a tendency toward distortion of the planar conformation upon complexing. As a result, the interaction between the conjugated dimethine groups is decreased. Furthermore, the formation of the *cis* structure should very greatly limit the interaction of the electron pair on the  $\text{NH}_2$  group with the pi electron system of the molecule. It seems quite likely that the electron pair on the  $\text{NH}_2$  group is divested of its conjugative influence upon complexing even in those cases where a planar chelate ring is formed. As a consequence of these considerations, the simplest modes of coordination to metal ions should produce shifts

in the position of the C=N stretching vibration toward higher frequencies. The position of the C=N absorption in the spectrum of  $[\text{Co}(\text{BdH})_2\text{Cl}_2]$  ( $1623\text{ cm.}^{-1}$ ) reflects the limiting effect of converting the biacetyldihydrazone molecule from the *trans* conformation to the *cis* conformation.

The slight displacement of the C=N absorption toward higher frequencies in the spectrum of  $[\text{Fe}(\text{BdH})_3]\text{I}_2$  (relative to the position of this absorption in the spectrum of biacetyldihydrazone) is a consequence of two opposing effects, the displacement toward higher frequencies which results from the forced *cis* conformation (as discussed above) and the displacement toward lower frequencies which results from metal-ligand pi-bonding. The hypothetical "lowering" attributed to metal-ligand pi-bonding is  $28\text{ cm.}^{-1}$  in this case.

The limiting position of the iron(II) complex with biacetyldihydrazone (in the series of complexes above) as indicated by the infrared spectra of the several complexes provides an additional illustration of the extreme degree of pi-electron interaction between the  $d^6$  iron(II) atom and the dimethine group,  $-\text{N}=\text{C}-\text{C}=\text{N}-$ .<sup>2,3,6</sup>

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[CONTRIBUTION FROM CHEMICAL LABORATORIES, GORAKHPUR UNIVERSITY, INDIA]

## Organic Compounds of Zirconium. VII. Studies in Zirconium Salicylates

BY R. N. KAPOOR AND R. C. MEHROTRA

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The reaction between zirconyl chloride and potassium salicylate has been studied by precipitation and titration (conductometric and electrometric) techniques. Further, the reactions of salicylic acid with zirconium tetrachloride and *isopropoxide* have been studied in anhydrous benzene medium. New zirconium compounds isolated are:  $\text{Zr}(\text{OPr-iso})_2(\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{O})$ ,  $\text{Zr}(\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2\cdot\text{Pr-isoOH}$ ,  $\text{Zr}(\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{O})_2$  and  $(\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{O})\text{Zr}(\text{OOC}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$ .

A detailed study of the mandelic acid derivatives of zirconium both by preparative as well as physico-chemical techniques has been described in recent publications<sup>1,2</sup> from these Laboratories. An extension of the above studies to other  $\alpha$ -hydroxy carboxylic (glycolic and lactic) acids revealed that the nature of conductometric and potentiometric titration curves was essentially similar to that described in the case of mandelic acid derivatives, although the products in general exhibited a much higher solubility. In view of the interesting results obtained with  $\alpha$ -hydroxy aliphatic carboxylic acids, it was considered worthwhile to make a study of salicylates also. It has been shown in the present investigation that the reaction between zirconyl chloride and potassium salicylate in aqueous solution yielded a precipitate corresponding in analysis almost to a monosalicylate  $\text{Zr}(\text{OH})_3(\text{salicylate})_{1.1}$  of zirconium. The conductometric and electrometric titrations of zirconyl chloride and potassium salicylate gave

curves (Fig. 1 and 2) similar to those described for titrations with potassium mandelate.<sup>2</sup> The electrometric titration of zirconyl chloride with potassium hydroxide was carried out in the presence of 1, 2 and 3 moles of potassium salicylate to estimate the extent of chelation (Fig. 3). The nature of the curves can be explained easily on the same lines as already described in the corresponding case of mandelic acid.

In view of the interesting results obtained on the physico-chemical studies of zirconium salicylates, it was considered of interest to study the system in non-aqueous medium also, where the complicating hydrolytic effects of water would be absent.

A preliminary reaction between zirconium isopropoxide and excess salicylic acid in benzene showed that almost all isopropylalcohol could be fractionated out azeotropically. The final zirconium compound thus formed, however, corresponded in analysis to zirconium trisalicylate only which might be represented by the first equation.

The same compound was obtained when zirconium tetrachloride in anhydrous benzene was treated with excess salicylic acid.

(1) R. N. Kapoor and R. C. Mehrotra, *J. Sci. Ind. Research (India)*, **16B**, 300, 304 (1957).

(2) R. N. Kapoor and R. C. Mehrotra, *THIS JOURNAL*, **80**, 3569 (1958).