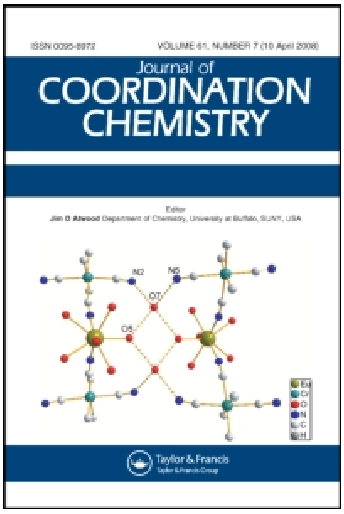

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VIBRATIONAL SPECTROSCOPIC STUDY OF BIS (BENZOYLBENZAMIDATE)Ni(II)

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The ligand benzoylbenzamide (HBBA) forms compounds with Ni(II) having the composition $Ni(BBA)_2.2H_2O$ and $Ni(BBA)_2$. The complex $Ni(BBA)_2$ can be isolated in red form or in a green form. The analysis of skeleton stretching bands indicated that the π electrons are not delocalized in the green compound. The structure is in this case tetrahedral or slightly distorted tetrahedral. The enthalpy of the red-green conversion is -13.0 kJ mol^{-1}, in accordance with the square-tetrahedral conversion energy, which is normally small.

INTRODUCTION

Various metal complexes with the chelating benzoylbenzamidate anion, $(PhCONCOPh)^-$, have been prepared with divalent and trivalent metals giving a neutral compound $M(PhCONCOPh)_n$.[1,2]

The complex of Ni(II) has two forms, a green paramagnetic form and a red diamagnetic form.[2] This behavior is similar to that observed with the $Ni(PhCOCHCOPh)_2$[3] but a basic difference is the presence of the imide group, -CONHCO-, in which the hydrogen is less acidic in comparison with the dibenzoylmethane. The smaller tendency of the π electron delocalization in the imide group is evident since several cationic complexes,[4,5] $M(RCONHCOR)_n^{2+}$ and neutral adducts such as $MCl_4(RCONHCOR)$[6] have been prepared.

The aim of this work is to analyze the vibrational spectral changes which occur when the red Ni(II) compound is converted to the green Ni(II) compound.

EXPERIMENTAL

The compound PhCONHCOPh was prepared by a method described in the literature[7] and the complex $Ni(BBA)_2.2H_2O$ following the procedure given in the *ref.* 2. The thermal stability of the complex was determined by thermogravimetric analysis (tga). We observe that the dehydration occurs at *ca.* 135° and that the anhydrous complex is stable up to *ca.* 190° when some decomposition begins. The anhydrous red and green compound were therefore obtained by heating the diaquo complex in vacuum (0.1 mmHg) at 40° and 140°, respectively. The green complex is better obtained by dissolving the red form in dry 1, 2-dichloroethane and then eliminating the solvent under vacuum.

The adduct $Ni(BBA)_2.2thf$ (thf = tetrahydrofuran) was obtained by adding a slight excess of thf to $Ni(BBA)_2$ dissolved in 1, 2-dichloroethane. The complex was filtered and dried under vacuum (Chemical Analysis: Ni = 9.18, C = 64.60, H = 5.31 and N = 4.20%; Expected: Ni = 8.96, C = 65.97, H = 5.54 and N = 4.27%).

Infrared (i.r.) spectra were obtained between 4000 - 180 cm^{-1} with a Perkin-Elmer model 180 spectrophotometer. Raman spectra were obtained with a Cary 82 Raman laser spectrophotometer using the 488.0 nm line of an Ar ion laser to excite the samples.

TABLE I

Infrared and Raman frequencies (cm^{-1})

Ni(BBA)$_2$.2H$_2$O		Ni(BBA)$_2$, red		Ni(BBA)$_2$.2thf Solid		Ni(BBA)$_2$.2thf Solution^b		
i.r.	Raman	i.r.	Raman	i.r.	Raman	i.r.	Raman	Assignments
1592s^a	1594vs	1589vs	1598vs	1596vs	1599vs	1595m	1600s	c
–	1557vs	–	1550s	–	1566m	–	1568m	ν_{CO}
1542vs	–	1525vs	–	1550vs	–	1554s	–	ν_{CO}
–	1492vs	–	1492m	–	1489m	–	1490m	c
1456vs	–	1456vs	–	1460vs	–	1457vs	–	c
1440w	1447s	–	1450m	–	1445m	1445sh	1448m	ν_{CO}
1415s, b	–	1420s, b	–	1420vs, b	–	–	–	ν_{CO}
–	1405m	1403s, b	1399w	–	–	–	–	ν_{CN}
1376vw	–	–	–	1378m	1380m	1389m	–	c
–	1344s	1358m	1364m	1340m	–	1361m	–	ν_{CN}
1336m	–	1334w	–	–	1334vs	1328m	1336s	ν_{CN}
1298w	1301m	1295w	–	1301vw	1299m	1289m	–	c

[a] v = very, s = strong, m = medium, w = weak, b = broad; [b] spectra in thf; [c] ring vibration.

Calorimetric measurements were made with a precision calorimeter LKB 8700-2 at a temperature of 25.00 ± 0.02°. The samples, weighing 3.00-9.00 mg, were sealed in a thin walled ampoule and broken in thf. The enthalpies of dissolution of both red and green Ni(BBA)$_2$ were determined for a series of samples.

RESULTS AND DISCUSSION

A square planar skeleton for Ni(-CONCO-)$_2$ would have D_{2h} point group symmetry and should show four carbonyl stretching vibrations, ν_{CO}, and four CN stretching vibrations, ν_{CN}. The cooordination of two ligands in axial positions, resulting in a trans-Ni(-CONCO-)$_2$Y$_2$ (where Y = a donor atom of the ligand) skeleton, does not change the symmetry but adds more two stretching vibrations of A_g and B_{1u} species.

The compound Ni(BBA)$_2$.2H$_2$O has Raman and i.r. spectra compatible with a D_{2h} symmetry skeleton. The stretching frequencies, mainly due to ν_{CO}, are observed at 1557, 1542, 1447 and 1415 cm^{-1} and the stretching frequencies mainly due to ν_{CN}, at 1405, 1344 and 1336 cm^{-1} (Tab. 1).

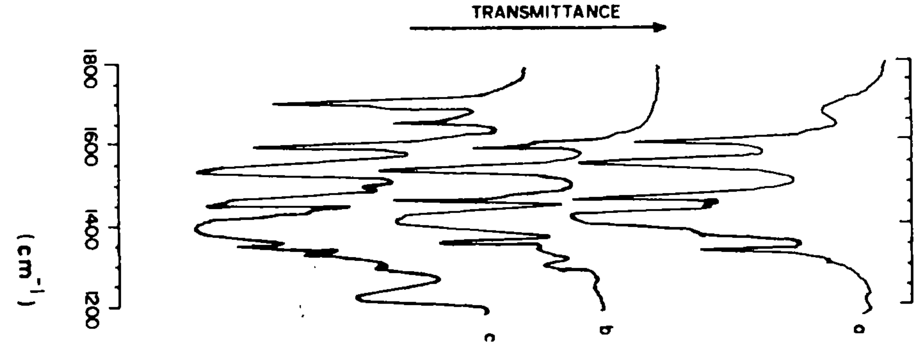

FIGURE 1 Infrared spectra of (a) Ni(BBA)$_2$.2H$_2$O, (b) Ni(BBA)$_2$, red, and (c) Ni(BBA)$_2$, green.

TABLE II
Infrared and Raman frequencies (cm^{-1}) of HBBA

Solid		Solution[a]	
i.r.	Raman	Raman	Assignments
3260s	3250vw		ν_{NH}
1725sh	1724m	1747m	imide I
1701vs	1700vs	1719m	
1674m	1677m	1690w	
1599m	1603vs	1600vs	b
1580m	1583sh		b
1502s	1495w		imide II
1462	–		b
1374m	–		b
1320w	1324w		ν_{CN}
1300m	1307w		b
–	1290m		b
1230vs	1235m		imide III

[a] spectrum in 1, 2-dichloroethane; [b] ring vibration.

Although the frequencies of the ligand bonded to the metal are not rigorously comparable with those of the free ligands, since in both case the vibrational coupling can be very different,[7] the observed frequency shifts, in a first approximation, are due to a higher π electron delocalization in the complex. In the free ligand, the imide I bands (ν_{CO}) appear at 1747 and 1719 cm^{-1} and the imide (III) band ($\nu_{CN} + \delta_{NH}$) at 1230 cm^{-1} (Tab. 2).

The vibrational spectra of the red compound $Ni(BBA)_2$ are similar to those of the diaquo compound (Tab. 1; Fig. 1a, 1b), indicating that both have the same symmetry of the skeleton. A spectral change occurs when the red compound is transformed to the green form. The i.r. and Raman spectra show a new band at *ca.* 1750 cm^{-1} (in solution (Fig. 1c; Tab. 3). The carbonyl stretching band is considerably shifted to higher frequency in 1, 2-dichloroethane. The other carbonyl stretching band appears at *ca.* 1550 cm^{-1}. Fig. 1c also shows that the green compound has a band at 1230 cm^{-1}, which also appears in the free ligand. In polar solvents such as thf, the vibrational spectra do show the ν_{CO} bands at *ca.* 1720 and at *ca.* 1740 cm^{-1} which indicates that in polar solvents the complex has the same skeleton as the red or diaquo complex. The complex isolated from this solution has the same structure.

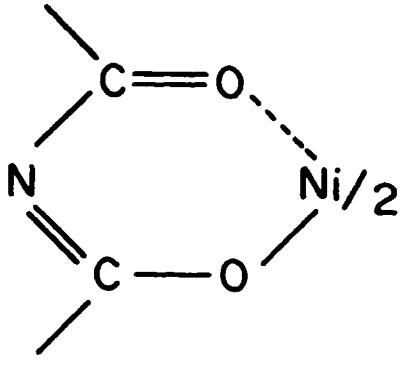

FIGURE 2

TABLE III
Infrared and Raman frequencies (cm^{-1}) of green $Ni(BBA)_2$

Solid		Solution[a]		
i.r.	Raman	i.r.	Raman	Assignments
1708vs	1710vw	1748m	1745vw	
1657m	–	1720m	1718m	ν_{CO}
1593vs	1599vs	1598s	1599vs	b
–	1550vs	–	1565m	
1537vs	–	1553s	–	ν_{CO}
1496w	1492s	1495vw	1491s	b
1465sh	–	1470s	–	b
1456vs, b	1448m	1450vw	1455sh	b
1395vs, b	1396m	1393vs	1390vw	ν_{CN}
1354w	1361vs	–	–	ν_{CN}
1331w	1335m	1334w	1336s	ν_{CN}
–	–	1312w	–	b
1295w	–	1283m	–	b
1229m	–	1232m	–	ν_{CN}

[a] i.r. and Raman spectra in 1, 2-dichloroethane; [b] ring vibration.

From the dissolution of $Ni(BBA)_2$ in the green and red forms in thf, the following enthalpies of dissolution were determined:

$$Ni(BBA)_{2\,(s,\,red)} + thf = Ni(BBA)_{2\,(thf)};\ \Delta H^\circ = -33.3 \pm 3.0\ kJ\ mol^{-1}$$

$$Ni(BBA)_{2\,(s,\,green)} + thf = Ni(BBA)_{2\,(thf)};\ \Delta H^\circ = -20.3 \pm 2.1\ kJ\ mol^{-1}.$$

The green form is thus slightly more stable than the red form.

CONCLUSION

From the vibrational spectroscopic data we conclude that the π electrons are not delocalized for the green compound, as shown in Fig. 2. This explains the shifts of the two ν_{CO} bands to 1708 and 1657 cm^{-1} and the presence of one ν_{CN} band at 1230 cm^{-1}. The electronic spectrum of the compound in 1, 2-dichloroethane showed one transition at 660 nm. In tetrahedral symmetry this transition can arise from the change from the $^3T_1(F)$ ground state to the $^3T_1(P)$ state. The enthalpy of the red-green conversion (-13.0 kJ/mol) is in accordance with square-tetrahedral or slightly distorted tetrahedral conversion energies, normally of few kJ/mol.[8]

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