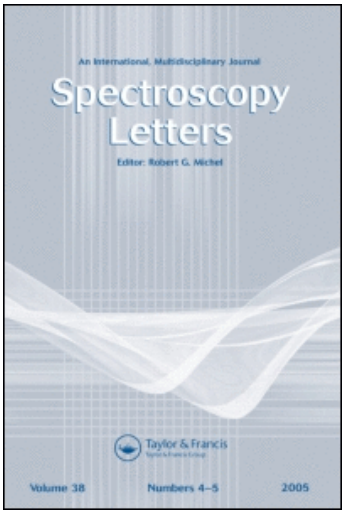

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared Study of the Heating Effects of Ni, Cd and Co Complexes of Sulfadimethoxine

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To cite this Article Topacli, A.(1999) 'Infrared Study of the Heating Effects of Ni, Cd and Co Complexes of Sulfadimethoxine', Spectroscopy Letters, 32: 5, 729 — 735
To link to this Article: DOI: 10.1080/00387019909350021
URL: http://dx.doi.org/10.1080/00387019909350021

SPECTROSCOPY LETTERS, 32(5), 729–735 (1999)

INFRARED STUDY OF THE HEATING EFFECTS OF Ni, Cd AND Co COMPLEXES OF SULFADIMETHOXINE

Keywords : Sulfadimethoxine, IR spectra, temperature effect.

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ABSTRACT

The Ni and new Cd and Co complexes of sulfadimethoxine (SDMX) are prepared and investigated their structural changes and stability by heating at different temperatures. The investigations were carried out by means of the infrared spectroscopy (IR) after heating the samples at several temperatures in the range 50-300 °C for an hour. The IR spectra of the heated samples at different temperatures have been compared with those at room temperature. The changes in the fundamental vibrational bands in their IR spectra gave the temperature values at which the samples decomposited. As a result, it is found that the stability of the complexes are higher than SDMX and their stability is in the order Ni > Co > Cd which depends on the second ionization potential of the metals.

INTRODUCTION

Sulfadimethoxine (SDMX) is a member of the sulpha family, an important class of molecules that have been thoroughly studied in terms of their pharmacological properties. However, although this molecule and its metal complexes play an important role in medical and biological fields, studies involving their IR spectra are scarce.

In our previous studies [1,2], we had reported the vibrational spectral data of SDMX and its nickel complex. The vibrational analysis indicated that the structural stability of the Ni $(SDMX)_2$ complex was higher than the free SDMX molecule by heating at different

temperatures. However, up to now, the structural stability of the metal complexes has not been reported.

In the present work, we have prepared new Co and Cd complexes of SDMX for the first time. It is considered that it would be of interest to undertake a detailed investigation of the effect of the heating on the molecular structure of SDMX and its metal complexes by infrared spectroscopy.

EXPERIMENTAL

Synthesis

The preparative methods for M $(SDMX)_2$ (M = Co, Cd) complexes were similar to those used for Ni $(SDMX)_2$ complex [1].

Analysis

Chemical analysis of the products for C, H, N and S were determined using an elemental analyzer. Co $(SDMX)_2$: found C = 42, H= 4, N = 15, S = 9 %. Calculated for Co $(C_{12}H_{14}N_4O_4S)_2$: C = 44, H = 4, N= 17, S = 10 %. Cd $(SDMX)_2$: found C = 39, H= 3, N = 15, S = 7 %. Calculated for Cd $(C_{12}H_{14}N_4O_4S)_2$: C = 39, H = 4, N= 15, S = 9 %.

Spectroscopic Measurement

Infrared spectra of the KBr pellet was recorded on a Perkin Elmer 621 instrument in the region 4000-400cm^{-1}.

RESULTS and DISCUSSION

It has been noted that the detailed IR data for the effect of temperature by heating on the sulfadimethoxine and its metal complexes are not plentiful in the literature. In our previous study [2], the IR spectra of SDMX and its Ni complex had been recorded after heating the samples at several temperatures in the range 50-280 °C.

In the present study, SDMX and M $(SDMX)_2$ (M = Co, Cd) are heated between 50 and 300 °C at a rate 10 °C/hour in an oven. The SDMX wavenumbers observed in the IR spectra of the heated samples at different temperatures have been compared with those at room temperature. By using the changes in the fundamental vibrational bands in their spectra, we found the temperature values at which the samples are decomposited. The assignment and wavenumbers of the observed SDMX bands in the IR spectra of the metal complexes are given in Table 1 at room temperature and their decomposition temperatures for comparison. The IR

TABLE 1.The fundamental vibrational wavenumbers (cm^{-1}) of SDMX in the $M(SDMX)_2$ (M = Ni, Co and Cd) at room and decomposing temperature.

SDMX		$Ni(SDMX)_2$		$Co(SDMX)_2$		$Cd(SDMX)_2$		Assignment
(room temp.)	(190°C)	(room temp.)	(300°C)	(room temp.)	(260°C)	(room temp.)	(240°C)	
3447	-	3357	-	-	-	3358	3347	ν(NH)
3345	3342	3254	3244	3260	-	3254	3262	ν(NH) $-SO_2NH$
3226	3195	3162	3156	3162	-	3163	3134	ν(NH) $-NH_2$
1651	1711	-	-	-	1672	-	1706	$\delta(NH_2)$
1594	1625	1594	1593	1594	1586	1593	1588	ν_{ring}
-	1548	1568	1564	1568	-	1567	1559	ν_{ring}
1489	1486	1487	1484	1487	1487	1488	-	ν_{ring}
1471	1471	1462	1456	1462	1462	1463	1457	ν_{ring}
1438	1446	1429	1429	1429	-	1429	-	$\delta(CH_3)$
1352	1357	1367	1376	1367	1331	1369	1345	$\delta(CH_3)$ $-OCH_3$
1314	1314	1275	1277	1275	1317	1271	1328	$\nu(SO_2)_{asy}$
1271	1266	1275	1277	1275	1266	1271	1258	ν(C-O) $-COCH_3$
1211	-	1211	1211	1211	-	1207	1220	ν(CCH)
1196	1182	1177	1174	1177	1192	1177	1201	$\nu(SO_2)_{sym}$
1137	1146	1140	1138	1140	1138 1132	1137	1148 1123	ν(CC)
1068	1066	1064	1059	1064	-	1064	-	δ(CCH) ν(CO)
1092	1086	1088	1086	1088	1086	1086	1084	δ_{ring}
990	992	996	993	996	992	1018	992	ν(CC) δ(CH) ν(CN)
879	-	883	881	883	-	878	876	ν(SN)
835	821	836	829	836	816	829	813	δ(CH)
812	-	810	807	810	-	812	-	δ(CCH)
789	-	781	-	781	-	784	-	$\rho(NH_2)$
726	719	735	733	735	718	732	718	γ(CNO)
685	678	687	683	687	677	686	677	ρ(CH) ν(CC) γ (CCC) γ (CNC)
621	-	623	-	623	-	-	-	γ (CH) γ (CNC) γ (CCN)
584	-	591	583	591	583	588	598	γ (CCC) γ (CNC)
560	560	572	570	572	568	566	568	$\rho(SO_2)$
536	535	545	538	545	538	546	536	$\delta(SO_2)$

spectra of the SDMX molecule and its metal complexes are given in FIG. 1-4, together at room and decomposition temperature. The elemental analysis of the Co and Cd complexes of SDMX suggests the general formula $M(II)(SDMX)_2$ (M = Co, Cd) for these compounds.

As seen from Table 1 and FIG. 1-4, the molecular structure of free SDMX and Ni, Co and Cd complexes are decomposited at 190 °C, 300 °C, 260 °C and 240 °C, respectively. In general, in the IR spectra of heated samples (FIG. 1-4), the intensities of some bands assigned to the ν_{ring} and $\nu(SO_2)$ stretching modes decrease. There is also a gradual decrease in intensity of the $\rho(NH_2)$ and γ_{ring} bands. In addition, $\nu(NH_2)$ stretching vibrations in the range 3500-3000cm^{-1} are overlapped with the broad peak assigned to the ν(OH) stretching mode of water arising after the samples are heated and cooled to the room temperature. In our previous study [1], $\delta(NH_2)$ vibrations had been observed at 1651cm^{-1} in the IR spectrum of free SDMX. This vibration showed a shift toward a lower wavenumber, but was overlapped with the broad peak assigned to the ring stretching mode of SDMX. This conclusion was based on the fact that one of the active binding sites of SDMX was the aminic group [1-5]. However, the $\delta(NH_2)$ band at 1651cm^{-1} shows a shift toward a higher wavenumber at 1711 cm^{-1} after SDMX are heated at 190 °C for an hour (Table 1). This band is shifted to 1672 and 1706 cm^{-1} in the IR spectra of Co and Cd complexes after they are heated at 260 °C and 240 °C, respectively. As seen from Table 1, the observed wavenumbers of $\delta(NH_2)$ band in the IR spectra of heated Cd and Co complexes approach to its position in the IR spectra of free SDMX. On the other hand, $\delta(NH_2)$ band observed in the IR spectrum of heated Ni complex has no significant shift in wavenumber compared to this band in the IR spectrum at room temperature. According to these results, it is considered that , M-N (metal-nitrogen) bond strength increases in the order of the metals second ionization potential. Thus, Ni complex is much more stable and Co and Cd complexes tend to break from the NH_2 group due to the effect of higher temperature.

In addition, as seen from Table 1, we also observed the wavenumber shift in the ring stretching mode at 1594 cm^{-1} of SDMX at room temperature in comparison to this band at 1625 cm^{-1} after heating at 190 °C for an hour. This vibration shows shifts toward lower wavenumbers at 1586 and 1588cm^{-1} in the IR spectra of Co and Cd complexes after they are heated at 260 °C and 240 °C, respectively. By comparing these values at room temperature, the observed shifts in the IR spectra of metal complexes are less than SDMX. In addition, the intensities of some bands assigned to the ring stretching modes decrease. Also the δ(CCH) band disappears due to the effect of temperature. Thus, it is considered that there is a deviation in the ring planes in the samples by heating.

In our previous study [1], we had also observed the wavenumber shifts in the asymmetric and symmetric modes of the SO_2 group of SDMX (near 1314 and 1196 cm^{-1}) in comprasion to those (near 1275 and 1177cm^{-1}) of the Ni complex. These bands were observed about 1314

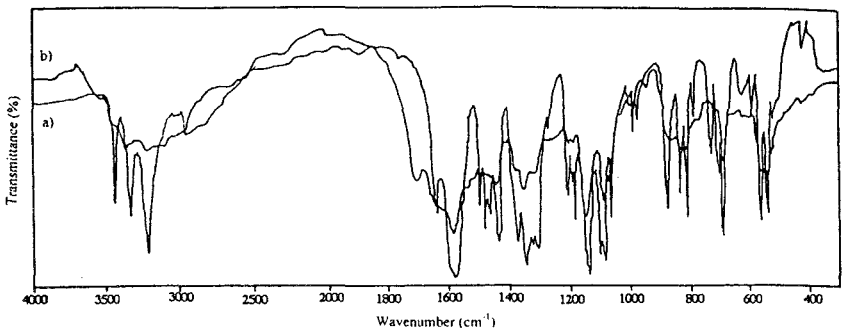

FIG. 1. Infrared spectrum of SDMX a) at room temperature b) after heating at 190 °C.

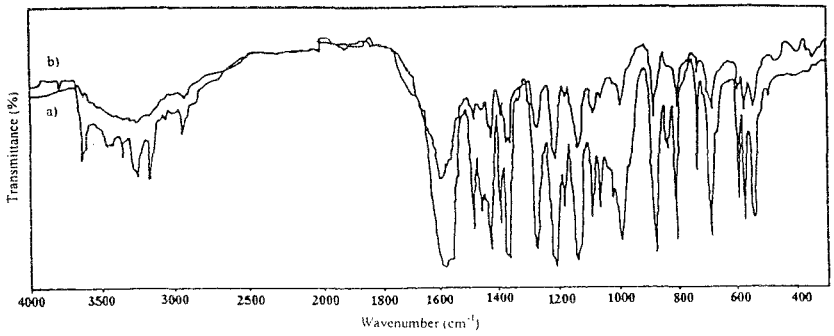

FIG. 2. Infrared spectrum of Ni $(SDMX)_2$ a) at room temperature b) after heating at 300 °C.

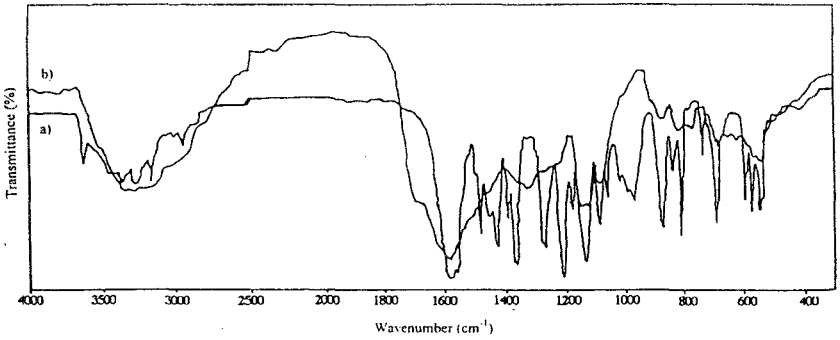

FIG. 3 Infrared spectrum of Co $(SDMX)_2$ a) at room temperature b) after heating at 260 °C.

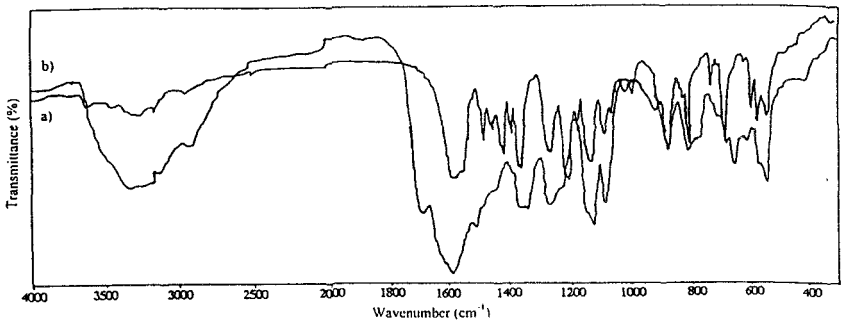

FIG. 4. Infrared spectrum of Cd $(SDMX)_2$ a) at room temperature b) after heating at 240 °C.

TABLE 2. The calculated bond lengths of M-N ve M-O (M = Ni, Co ve Cd)

Bonds	Average bond lengths (Å)	Bonds	Average bond lengths (Å)
Cd-N	2.09	Cd-O	2.14
Co-N	1.78	Co-O	1.82
Ni-N	1.77	Ni-O	1.81

and 1182cm^{-1} (as the same values at room temperature) respectively, in the IR spectra of SDMX after heating at 190 °C. Similarly, we observed these vibrations at 1277 and 1174 cm^{-1} (as the same values at room temperature) in the IR spectra of Ni $(SDMX)_2$ after heating 300 °C. However, in the IR spectra of Cd and Co complexes, these modes have no shifts in wavenumber compared to those in the IR spectra of SDMX after heating at 190 °C. So it is considered that the molecular structures of metal complexes also tend to break from the SO_2 group.

By using the geometry optimization, the calculated M-N and M-O bond lengths of the samples are represented in Table 2. The vibrational analysis indicate that the structural stability of M $(SDMX)_2$ (M = Ni, Co, Cd) complexes are higher than SDMX molecule. As seen from Table 2, the Ni-N and Ni-O bond lengths are shorter than those of Co and Cd,

respectively. Their stabilities are in the order Ni > Co > Cd, which are in agreement with the increasing order of the second ionization potential of these metals.

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Date Received: February 4, 1999
Date Accepted: June 1, 1999