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Studies on the Disposition of Carbonato Group in Cobalt(III) Complexes

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Experimental data on the charge transfer band position of various carbonato complexes of the general formula $[Co(N_4)Co_3]^+$ $(N_4=(NH_3)_4$, $(en)_2$, $(pn)_2$, $(tn)_2$, cis$[Co(NH_3)_2(CO_3)_2]^-$ *and* $[Co(CO_3)_3]^{3-}$ *and the vibrational frequencies of carbonyl group as well as the N–H stretching frequencies have been obtained. By comparing the ultraviolet band maxima of the carbonato complexes with those of sodium carbonate (purely ionic) and propylene carbonate (purely organic) covalency factors have been evaluated and compared with covalency factors obtained from carbonyl stretching frequencies, which shows a reasonable agreement. Examination of the infrared spectra of both deuterated and undeuterated complexes of* $[Co(NH_6)_3]^{3+}$, $[Co(NH_3)_5CO_3]^+$ *and* $[Co(NH_3)_4CO_3]^+$ *shows the presence of intramolecular hydrogen bonding between the ammine protons and the oxygen atom of the free end of the carbonate ligand of the type N–H...O in* $[Co(NH_3)_5CO_3]^+$ *complex. The covalency factors for the carbonato and oxalato complexes conclusively show that the carbonato complexes are more reactive than the oxalato complexes which is in good agreement with the experimental findings.*

Introduction

Carbonate is an interesting ligand which is capable of acting both as a bidentate and a monodentate in metal complexes. Recently the chemistry of metal carbonato complexes has been reviewed.[1] The modest success of the average field model in the interpretation of the electronic spectra of carbonato and oxalato complexes of Co^{III} has been pointed out by Sastri and Langford.[2] In this communication we wish to report the vibrational spectral data of the carbonato complexes and discuss some of the important features of the carbonate ligand in the Co^{III} complexes.

Experimental

Na_2CO_3 and propylene carbonate were of reagent grade. All the carbonato ammine Cobalt(III) complexes were prepared according to standard procedures.[3,4]

The deuterated compounds were prepared by dissolving the complex in 99.9% D_2O and evaporating to dryness for at least three times.

The vibrational spectra of samples in KBr discs were recorded on Perkin-Elmer Model 225 Infrared Spectrophotometer. The charge transfer bands were recorded on Cary Model 15 recording uv-visible spectrophotometer.

Results

Data on the charge transfer bands of the complexes are tabulated in table I. Vibrational stretching frequencies of the carbonyl group are collected in table II and the N–H frequencies are presented in table III. Figure 1 represents the linear relationship between carbonyl group stretching frequency and the C=O bond length.

Discussion

Charge transfer bands. In an earlier paper[2] the relationship between the charge transfer band and the low energy ligand field band ($^1A_{1g} \rightarrow {}^1T_{1g}$) showed a correlation slope of unity which fitted into the interpretation that the charge transfer transition of the electron from ligand (π) to the metal (eg) type, in the family of carbonato complexes ranging from $[Co(NH_3)_5CO_3]^+$ to $[Co(CO_3)_3]^{3-}$. The data in Table I represent the charge transfer band maxima of ionic carbonate, organic carbonate and a family of carbonato cobalt(III) complexes along with the calculated covalency factors. In the calculation of covalency factors the peak of sodium carbonate is assumed to have a full share of ionic character and the propylene carbonate to be fully covalent in nature, which is a reasonable assumption to make. On an average, carbonate as a bidentate ligand in the Co^{III} complexes appears to possess 44% of covalent character. The complex $[Co(NH_3)_5CO_3]^+$ where carbonate is a monodentate ligand exhibits about 35% covalent character, which is much more than the expected value of about 22% for a monodentate carbonato complex since a bidentate complex exhibits 44% covalent character. The observed covalency character of 35% for $[Co(NH_3)_5CO_3]^+$ shows a greater degree of biden-

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[1] K.V. Krishnamurty, G.M. Harris and V.S. Sastri, *Chem. Rev.*, *70*, 171 (1970).
[2] V.S. Sastri and C.H. Langford, *Can. J. Chem.*, *47*, 4237 (1969).
[3] V.S. Sastri, Ph.D. Thesis, State University of New York at Buffalo, Buffalo, New York, 1966.
[4] R.J. Dobbins and G.M. Harris, *J. Amer. Cehm. Soc.*, *92*, 5104 (1970).

Table I. Ultraviolet Absorption Maxima and Vovalency Factors of Carbonato Complexes of Co^{III}.

Complex	Absorption band Maximum (nm.ı	Covalency Factor	Reference
Na_2CO_3	213	0.0	This work
$[Co(NH_3)_5CO_3]^+$	233	0.35	»
$[Co(NH_3)_4CO_3]^+$	238	0.44	»
$[Co(en)_2CO_3]^+$		0.44	»
$[Co(pn)_2CO_3]^+$	238	0.44	»
$[Co(tn)_2CO_3]^+$	238	0.44	»
cis-$[Co(en)(NH_3)_2CO_3]^+$	243	0.53	4
trans-$[Co(en)(NH_3)_2CO_3]^+$	235	0.39	4
Propylene Carbonate	270	1.00	This work

Table II. Carbonyl Stretching Frequencies and Covalency Factors of Carbonato Complexes of Co^{III}.

Complex	$\nu_{C=O}$, cm^{-1}	Covalency Factor	Reference
$[Co(NH_3)_4C_2O_4]^+$	1705	0.57	This work
$[Co(NH_3)_4CO_3]^+$	1592	0.44	»
$[Co(en)_2CO_3]^+$	1628	0.54	»
	1615	0.50	
$[Co(pn)_2CO_3]^+$	1575	0.40	»
$[Co(tn)_2CO_3]^+$	1575	0.40	»
$[Co(NH_3)_2(CO_3)_2]^-$	1623	0.52	4
$[Co(CO)_3)_3]^{3-}$	1590	0.44	This work
CO_3^{2-} in calcite	1415-1430	0.00	8
Ethylene Carbonate	1805	1.00	This work

Table III. I.R. Data on N-H Vibrational Frequencies ($cm.^{-1}$).

Complex	ν_{NH_3}	δ_d (NH_3)
$[Co(NH_3)_6](NO_3)_3$	3295, 3200	1350 (broad)
$[Co(ND_3)_6](NO_3)_3$	2460, 2320	1360
$[Co(NH_3)_5CO_3]NO_3$	3300, 3190, 3115	1362.5
$[Co(ND_3)_5CO_3]NO_3$	2420, 2375	—
$[Co(NH_3)_4CO_3]NO_3$	3300, 3200	1367

tate character of the carbonato group and the only valid explanation is that there is a possible intramolecular hydrogen bonding between the ammine proton and the uncoordinated oxygen atom of the free end of the carbonato group or intermolecular hydrogen bonding. Another feature of these data is that *trans*–$[Co(NH_3)_2(en)(CO_3)]^+$ is less covalent (39%) than the corresponding geometric *cis* isomer (53%) and this is also reflected in the aquation rates of these complexes. *Trans*–$[Co(NH_3)_2(en)(CO_3)]^+$ aquates as well exchanges with free $^{14}CO_3^{2-}$ much faster than the corresponding *cis* isomer.[4,5]

Infrared Vibrational Spectra. Only the carbonyl stretching frequencies of the ionic carbonate, organic carbonate and complex carbonates of Co^{III} along with the covalency factors are given in Table II. The covalency factors were calculated assuming sodium carbonate and propylene carbonate are purely ionic and covalent respectively. Similar calculations have been done earlier.[6] With the exception of one or two complexes the covalency factors center around a value of 0.45 which is about 45% covalent character for carbonate in cobalt(III) complexes. The agreement between the percent covalent character by using data from charge transfer spectra and infrared vibrational spectra, is very good. Now a comparison of the covalency character of $[Co(NH_3)_4C_2O_4]^+$ complex

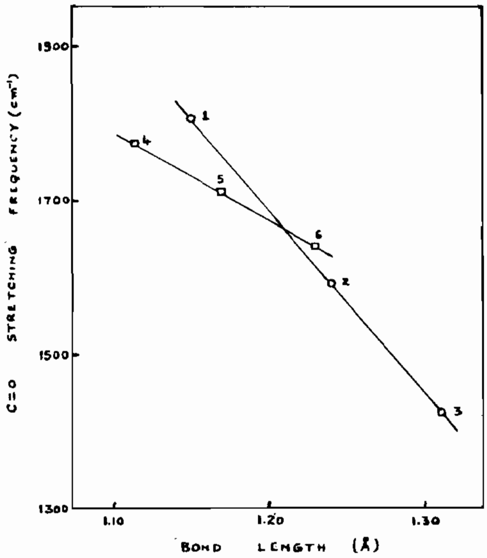

Figure 1. C=O stretching frequency (cm^{-1}) plotted against C=O length (Å). ○ represents carbonates - 1. Ethylene carbonate 2. $Co(NH_3)_4CO_3^+$ 3. Calcite □ represents oxalates 4. Dimethyl oxalate 5. $Cr(C_2O_4)_3^{3-}$ 6. Sodium oxalate.

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(5) T.P. Das Gupta and G.M. Harris, *J. Amer Chem. Soc.*, *93*, 91 (1971)

(6) M. J. Schmelz, T. Miyazawa, S. Mizushima, T.J. Lane and J. V. Quagliano, *Spectrochim. Acta*, *9*, 51 (1957).

(0.57) with that of $[Co(NH_3)_4CO_3]^+$ ion (0.44) shows definitely that Co–O bond in oxalate complex should be much more stable than the corresponding metal-oxygen bond in carbonato complex, which is understandable in view of the steric strain present in the carbonato complex.

In Figure 1, the stretching frequencies of the carbonyl group in carbonates and oxalate in ionic, complex and organic compounds are plotted against the $C=O$ bond distances collected from x-ray data available in the literature. Surprisingly the linearity observed in the plots is very good. It is important in this regard to point out a similar correlation obtained by Rundle and co-workers in hydrogen bonded systems like organic acids[7,8] in spite of the fact, that this correlation implies the assumption that the vibration involves only the carbon and oxygen atoms relative to each other with no other motion of the molecule. This assumption should in principle not be applicable for carbonate grouping due to the splitting of the stretching frequency into symmetric and asymmetric modes.

The N–H stretching, degenerate bending and the N–H symmetric deformation frequencies of both the deuterated and undeuterated complexes are given in Table III. The N–H stretching frequencies are shifted to lower values on deuteration as expected. Two N–H stretching bands were observed in the case of $[Co(NH_3)_6]^+$ and $[Co(NH_3)_4CO_3]^+$ complexes, while three bands were clearly identified in the case of $[Co(NH_3)_5CO_3]^+$ and in addition the bands occur at lower frequencies. These data support the presence of either intramolecular or intermolecular hydrogen bonding of the type N–H–O in $[Co(NH_3)_5CO_3]^+$ complex. Crystal structure data on $[Co(NH_3)_5CO_3]^+$ support the presence of intramolecular hydrogen bonding in this complex.[9]

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(7) R.E. Rundle and M. Parasol, *J. Chem. Phys.*, *20*, 1487 (1952).
(8) M. Margoshes, F. Fillwalk, V.A. Fassel and R.E. Rundle, *J. Chem. Phys.*, *22*, 381 (1954).
(9) H.C. Freeman and G. Robinson, *J. Chem. Soc.*, 3194 (1965).
(10) K. Nakamoto, I.R. Spectra of inorganic and coordination compounds, 2nd ed., John Wiley and Sons, N.Y. 1969.