Contribution from the Fordham University, Bronx, N.Y., and Iona College, New Rochelle, N.Y., U.S.A.

The Preparation of the Bidentate Urea Complex $[Co(urea)_4](NO_3)_2$

P.S. Gentile, P. Carfagno, S. Haddad, and L. Campisi

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The complex $[Co(urea)_4](NO_3)_2$ was synthesized. Analysis of the infrared and ultraviolet spectra revealed the presence of urea complexed as a monodentate and a bidentate ligand. Tentative band assignments are given for both complexing modes of urea. An unassigned band occurring at 932 cm^{-1} may be diagnostic for the presence of bidentate urea.

Introduction

Efforts have been directed in the past to preparation and structural studies of urea complexes.[1] Previous work[2] has indicated this rather weak ligand bonds at either one of two possible sites, oxygen or nitrogen; however, compounds with bidentate or bridging urea have not been reported. Since other planar ligands, geometrically similar to urea (C_{2V} symmetry), such as NO_3^- and CO_3^{2-} (D_{3h}), can bond in a bidentate fashion, it was of considerable interest to ascertain whether such urea complexes could also be prepared.

Experimental Section

$[Co(urea)_4](NO_3)_2$. Stoichiometric quantities of $Co(NO_3)_2 \cdot 6H_2O$ and urea in the mole ratio of 1:4 were placed in a mortar and ground after the addition of a few drops of methanol. The reaction mixture was then dried *in vacuo*. This process was repeated until all of the water of hydration was driven off.

Anal. Calcd. for $[Co(urea)_4](NO_3)_2$: Co, 13.93. Found: 13.80

$[Co(urea)_4(H_2O)_2](NO_3)_2$. Stoichiometric quantities of hexahydrated cobaltous nitrate and urea were dissolved in a 50% water-ethanol mixture in a 1:4 mole ratio. Large crystals developed upon evaporation of the solvent.

Anal. Calcd. for $[Co(urea)_4(H_2O)_2](NO_3)_2$: Co, 12.84. Fond: 12.82.

Conversion of $[Co(urea)_4(H_2O)_2](NO_3)_2$. The dihydrate upon standing in vacuo converts to the anhydrous componud. The infrared spectrum and powder diffraction pattern of this resultant compound was identical with those for the $[Co(urea)_4](NO_3)_2$ previously prepared.

Physical Measurements. Infrared spectra were obtained from Nujol and fluorocarbon mulls on a Perkin-Elmer 337 infrared spectrophotometer. The visible spectra of the solid complexes. suspended in Nujol, was recorded using a Cary 15 spectrophotometer.

Results and Discussion

The electronic spectra for $[Co(urea)_4](NO_3)_2$ and $[Co(urea)_4(H_2O)_2](NO_3)_2$, Figure 1, are consistent with that for weak field octahedral cobalt complexes.

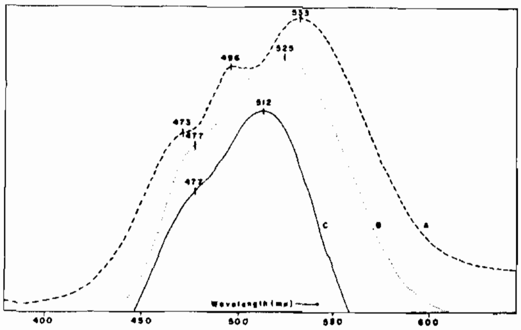

Figure 1. Visible spectra of (A) $[Co(urea)_4(NO_3)_2$ - - - - -, (B) $[Co(urea)_4(H_2O)_2](NO_3)_2$ . . . . . , (C) $Co(H_2O)_6^{2+}$ ———.

Examination of the infrared spectrum for the anhydrous compound, Fig. 2, and table I reveals that the NO_3^- groups are present in ionic form, consequently only urea molecules are involved in coordination. However, in order to satisfy the octahedral coordination of cobalt, the stoichiometry of the compound dictates that urea cannot be present solely as monodentate ligands. Among the many interesting structural possibilities which can be postulated for this compound, one is suggested in which there are two monodentate and two bidentate chelating or bridging urea molecules per cobalt atom. Interpretation of the infrared spectrum of $[Co(urea)_4](NO_3)_2$ is agreement with this model.

Previous studies have shown that urea conventio-

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[1] Gentile P.S. and Campisi L.S., *J. Inorg. Nucl. Chem.*, *27*, 2291 (1965). Gentile P.S., Campisi L.S., and Carfagno P., *J. Inorg. Nucl. Chem.*, *28*, 1143 (1966).

[2] Penland R.B., Mizushima S., Curran C., and Quagliano J.V., *J. Am. Chem. Soc.*, *79*, 1575 (1957).

Table I. Infrared Absorption Frequencies for [Co(Urea)$_4$](NO$_3$)$_2$.

3455	S	antisym. stretch. free NH$_2$ of O-bound urea
3400	M	antisym. stretch. free NH$_2$ of bidentate urea
3350	sh	sym. stretch. free NH$_2$ of O-bound urea
3320	S	sym. stretch. free NH$_2$ of bidentate urea
3260	S	low frequency NH peak obs. in solid state urea
3220	S	antisym. stretch. bound NH$_2$ of bidentate urea
3135	M	sym. stretch. bound NH$_2$ of bidentate urea
1685	sh	NH$_2$ bend. and CO stretch. of bidentate urea
1670	S	
1640	sh	free NH$_2$ bend. and CO stretch. of monodentate urea
1625	S	
1590	S	bound NH$_2$ bend. of bidentate urea
1565	S	unassigned mode of monodentate urea
1555	sh	
1501	M	NCN antisym. stretch. of monodentate urea
1466	M	NCN antisym. stretch. of bidentate urea
1351	S	NO$_2$ stretch. of nitrate ion
1220	M	free NH$_2$ rock. of monodentate and bidentate urea,
1155	M	and coordinate NH$_2$ wagging
1109	W	
1025	M	NO stretch. of ionic nitrate and NCN sym. stretch of urea
1010	M	
932	M	unassigned mode of bidentate urea
818	W	out-of-plane bend. of ionic nitrate
785	W	unassigned mode of bidentate and monodentate urea
758	W	

nally complexes with cobalt via the oxygen atom[2,3]. For the multitude of bands occuring in the infrared spectrum of [Co(urea)$_4$](NO$_3$)$_2$, absorptions can be discerned which completely account for oxygen-to-metal bonding[2], indicating the presence of monodentate urea. For the remaining absorptions, plausible assignment can be made if bidentation is assumed, where for each of the remaining two ureas, both oxigen and nitrogen-to-metal bonding exists.

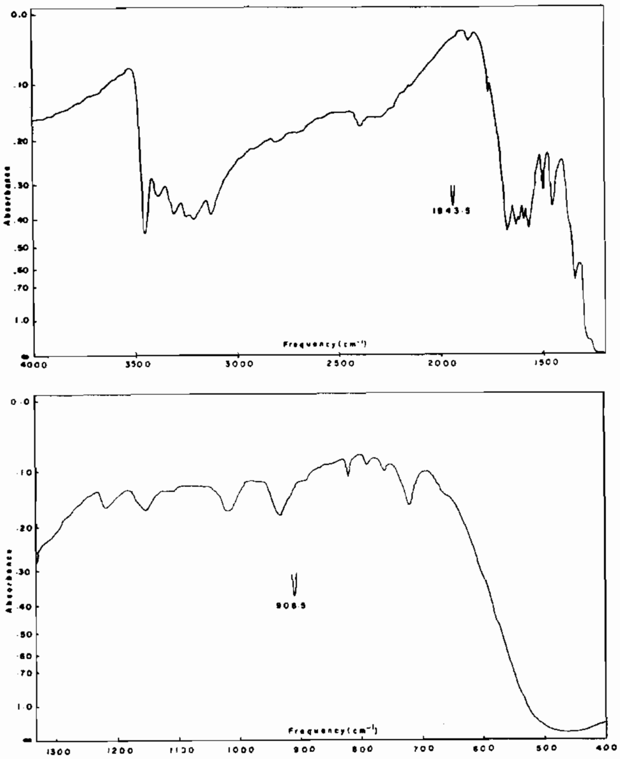

Figure 2. Infrared spectrum of [Co(urea)$_4$](NO$_3$)$_2$.

For the two differenly bound urea molecules, the monodentate and the bidentate, one anticipates a total of six absorption bands in the NH$_2$ stretching region. The asymmetric and symmetric stretch absorptions are associated with the monodentate ligand and these occur at 3455 and 3350 cm^{-1} respectively. For the bidentate donor a total of four bands are contributed, two for the free or non-bonded NH$_2$ stretch (antisym. and sym.), found at 3400 and 3320 cm^{-1}, and two of the coordinated nitrogen NH$_2$ stretch (antisym. and sym). These latter vibrations are located at 3220 and 3135 cm^{-1}. The last band is approximately 100 cm^{-1} higher than found when only pure nitrogen to metal bonding exists. However. one may ascribe this difference to either weaker N-to-metal bonding or alteration. of vibrational frequency owing to bidentation. Finally an additional band is noted around 3260 cm^{-1}. However this unassigned absorption also appears in urea spectra in the solid state. The assignments for NH$_2$ frequencies for the seven absorptions which are observed are listed in Table I; however, because of band overlap, and different extinctions, the assignments at 3350, 3320, and 3260 cm^{-1} are tentative.

[3] Unpublished Data.

In the 1700-1400 cm^{-1} region those absorptions centered about 1640, 1565, and 1500 cm^{-1} agree well with data for monodentate, oxygen-to-metal bonding. The bands occuring around 1680 cm^{-1}, however, are assigned to the couple CO stretch and NH_2 bend of the bidentate ligand. These bands appear to be essentially unshifted when compared to uncomplexed urea. This is not unexpected since the opposing effects of electron demand by both donor oxygen and nitrogen atoms would tend to cancel, so that the carbonyl double bond character is practically unaltered. The multiplicity of the CN bond in this region is also basically unchanged as discerned from the absorption frequency of the NCN vibration. The NCN asymmetric stretch appears at 1473 cm^{-1} in free urea, and 1460 cm^{-1} in the complex.

Finally, in the region around 1150 cm^{-1} three absorptions are expected, two associated with free NH_2 rocking from monodentate urea, and one band related to coordinated NH_2 wagging vibration. The infrared spectrum of the complex shows these bands at 1220, 1155 and 1109 cm^{-1}.

In the absence of the fully deuterated sample some of the assignments made thus far can only be tentative, howver, the validity of the model formulated can be further substantiated by examination of the infrared spectrum of $[Co(urea)_4(H_2O)_2](NO_3)_2$. This octahedral complex, in which the urea ligands are typically oxygen bound, upon dehydration, is converted to $[Co(urea)_4](NO_3)_2$. As coordinated water molecules are removed, nitrogen atoms also assume positions on the coordination sphere and new bands, associated with bidentate urea, appear in the spectrum.

As one final note, it should be observed that a rather prominent band at 932 cm^{-1} appears in the spectrum of the bidentate sample. Although no assignment is made for this band, its origin is probably analogous to the absorption at 900 cm^{-1} which appears only in the case of N bound urea. It may be that the absorption at 932 cm^{-1} which appears to be indicative of weaker nitrogen atom bonding, may also be diagnostic of bidentate urea.

It may be noted that two of us (P.S.G. and S.H.) have undertaken the crystal structure determination of $[Co(urea)_4](NO_3)_2$. The results of this are sufficiently advanced to indicate that bidentation of urea does indeed occur.

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