

(II) PREPARATION AND CHARACTERIZATION OF MN (III) COMPLEXES

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Abstract

We have prepared and characterized a few Mn (III) complexes by using a few bidentate and tridentate ligands. Spectra of the manganese (III) ion in a variety of molecular environments are reported. On the basis of solution spectra, some of these complexes seem to be typically distorted.

Introduction

The d^4 , manganese (III) ion has a 5D field free ground term level which, in an octahedral field, splits into a 5E_g ground term and a ${}^5T_{2g}$ excited term. However, the Jahn-Teller theorem predicts that an octahedral complex will distort in order to remove the orbital degeneracy of the ground term. Because the orbital degeneracy lies in the e_g orbitals, the ground term splitting is expected to be larger than that of the excited term. Therefore, the ground electronic term anticipated in octahedral complexes, 5E_g , is subject to strong Jahn-Teller forces [1]. In general, the three absorption bands observed in the visible region of the electronic spectra have been satisfactorily assigned in term of D_{4h} symmetry [1,2]. A few crystal structures for Mn (III) complexes containing six chemically equivalent donor atoms are available for consideration of Jahn-Teller effects.

Indeed, there are a significant number of structures reported for manganese (III) complexes which purport to demonstrate the existence of an axial distortion. We have recently prepared [3], a mononuclear manganese (III) complex containing monofunctional ligand, $[Mn(Urea)_6] (C_{10}_4)_3$, which has been used over a

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period of years as a reagent in the synthesis of a variety of manganese (III) complexes.

We have recently synthesized Bis (2,2',2''-Terpyridine) manganese (III) perchlorate and Tris (Picolinato) manganese (III) monohydrate complexes [4].

In this work, we have reported preparation and characterization Tris

$[2,6\text{-Pyridine dicarboxylato} = (1\text{-})\text{-}N^1, 0^2]$ manganese (III); Pyridinium bis (2,6-Pyridine dicarboxylato) manganate (III); Aqua

$[2,6\text{-Pyridine dicarboxylato} = (1\text{-})\text{-}N^1, 0^2]$

$[2,6\text{-Pyridine dicarboxylato} = (2\text{-})\text{-}N^1, 0^2, 0^6]$ manganese (III).

Experimental Section

A) Preparation

1) Preparation of $[Mn(Urea)_6] (C_{10}_4)_3$

As shown in a previous paper [4], crystals of the composition $[Mn(Urea)_6] (C_{10}_4)_3$ can be easily obtained. We have used this complex as a reagent in the synthesis of a variety of manganese (III) complexes.

2) Preparation of $[Mn(PyDCH)_3]$

0.71 g (1×10^{-3} mole) hexakis Urea manganese (III)

perchlorate and 0.50 g (3×10^{-3} mole) 2,6-pyridine dicarboxylic acid were dissolved in 80 ml absolute ethanol. The mixture was stirred for 3 hrs. A redish microcrystalline solid formed and was separated by filtration, washed with absolute ethanol, and placed in a desiccator over CaCl_2 . Anal. Cald for $[\text{Mn}(\text{PyDCH})_3]$: H, 2.19; Mn, 9.93; O, 34.70. Found: H, 2.31; Mn, 9.80; O, 34.90. Therefore, this ligand acts as a bidentate ligand.

3) Preparation of $\text{PyH}[\text{Mn}(\text{DPA})_2]$

0.71 g (1×10^{-3} mole) hexaKis Urea manganese (III) perchlorate and 0.50 g (3×10^{-3} mole) 2,6-pyridine dicarboxylic acid were dissolved in 80 ml absolute ethanol. During stirring, the mixture was added to the pyridine drop by drop. A purple microcrystalline solid formed and was separated by filtration, washed with absolute ethanol, and placed in a desiccator over CaCl_2 . Anal. Cald for $\text{PyH}[\text{Mn}(\text{DPA})_2]$: C, 49.0; H, 2.6; Mn, 11.8; N, 9.0. Found: C, 49.0; H, 2.6; Mn, 10.9; N, 8.5. Therefore, this ligand acts as a tridentate ligand.

4) Preparation of $[\text{Mn}(\text{PyDCH})(\text{PyDC})(\text{H}_2\text{O})]$

0.33 g (2×10^{-3} mole) 2,6-pyridine dicarboxylic acid and 0.23 g (1×10^{-3} mole) manganese (III) acetate were dissolved in 40 ml absolute ethanol. The mixture was stirred for 60 min. A violet microcrystalline solid formed which was separated by filtration, washed with absolute ethanol, and placed in a desiccator over CaCl_2 . Anal. Cald for $[\text{Mn}(\text{PyDCH})(\text{PyDC})(\text{H}_2\text{O})]$: C, 41.6; H, 2.3; Mn, 13.6; O, 35.6; N, 6.9. Found: C, 41.6; H, 2.7; Mn, 14.5; O, 35.1; N, 6.6. Therefore, this ligand acts as a bidentate and tridentate ligand.

B) Infrared Spectra

The IR spectrum of the $[\text{Mn}(\text{Urea})_6](\text{ClO}_4)_3$ has been studied in a previous paper [4].

In the IR spectrum of $[\text{Mn}(\text{PyDCH})_3]$, a broad band in 3400 cm^{-1} belongs to O-H stretching vibration. The presence of some bands in the $1650\text{-}1420 \text{ cm}^{-1}$ region could be assigned to C=C and C=N stretching vibrations. The C=O stretching frequency appears at 1650 cm^{-1} . The C-O stretching frequency appears at 1320 cm^{-1} . Two bands at 770 and 740 cm^{-1} are assignable to the out of plane bending vibration of C-H group. Also one band at 450 cm^{-1} and another band at

430 cm^{-1} could be assigned to the stretching vibration of Mn-N and Mn-O bonds.

In the IR spectrum of $\text{PyH}[\text{Mn}(\text{DPA})_2]$, the C-H stretching frequency appears at 3080 cm^{-1} . A broad band at 1650 cm^{-1} belongs to C=O stretching vibration. The presence of some bands in the $1600\text{-}1550 \text{ cm}^{-1}$ region could be assigned to C=C and C=N stretching vibrations. The C-O stretching frequency appears at 1300 cm^{-1} . Two bands at 740 and 760 cm^{-1} are assignable to the out of plane bending vibration of C-H group. Also two bands at 450 and 430 cm^{-1} could be assigned to the stretching vibration of Mn-N and Mn-O bonds.

In the IR spectrum of $[\text{Mn}(\text{PyDCH})(\text{PyDC})(\text{H}_2\text{O})]$, a broad band in 3400 cm^{-1} presents the O-H stretching vibration. The C-H stretching frequency appears at 3060 cm^{-1} . A band in 1650 cm^{-1} belongs to the stretching vibration of the carbonyl group and presents the structure of $\text{C}=\overset{\text{O}}{\text{C}}_{\text{O-M}}$ in the complex. The presence of some bands in the $1650\text{-}1420 \text{ cm}^{-1}$ region could be assigned to C=C and C=N stretching vibrations. The C-O stretching frequency appears at 1315 cm^{-1} . Two bands at 750 and 700 cm^{-1} are assignable to the out of plane bending vibration of C-H group. Also two bands at 460 and 420 cm^{-1} could be assigned to the stretching vibration of Mn-N and Mn-O bonds.

C) Ultraviolet and Visible Spectra

All ultraviolet spectra are summarized in Table 1, showing presence of ligands in their complexes. All visible spectra are summarized in Table 2. In all cases, there are two absorption bands in the visible region. The presence of two bands in the present complexes indicates a lowering of the symmetry due to Jahn-Teller distortion.

Conclusion

On the basis of solution spectra data, one complex seems to be typically distorted. Considering the effective symmetry in a chelate system such as $\text{M}(\text{AA})_3$ or $\text{M}(\text{AB})_3$ in solution which is actually the same as an MX_6 system, i.e., O_h symmetry, only one spin allowed absorption band (${}^5\text{E}_g \longrightarrow {}^5\text{T}_{2g}$) is to be expected in approximately visible region.

Table 1. Ultraviolet absorption bands of Mn(III) Complexes

Complex	(cm^{-1})	ϵ (lit mole $^{-1}$ cm $^{-1}$)
[Mn (Urea) $_6$] (C10 $_4$) $_3$	48,309	2,843
	38,642	2,143
	29,412	1,157
[Mn (PyDCH) $_3$]	47,169	25,000
	37,878	10,555
PyH [Mn (PyDC) $_2$]	47,619	20,465
	39,370	9,767
[Mn (PyDC) (PyDCH) (H $_2$ O)]	45,871	10,714
	38,461	8,392

Table 2. Visible absorption bands of Mn (III) Complexes

Complex	(cm^{-1})	ϵ (lit mole $^{-1}$ cm $^{-1}$)
[Mn (Urea) $_6$] (C10 $_4$) $_3$	13,888	72
	19,600	179
[Mn (PyDCH) $_3$]	19,685	169
	20,833	144
PyH [Mn (PyDC) $_2$]	20,000	172
	20,920	158
[Mn (PyDC) (PyDCH) (H $_2$ O)]	20,080	347
	20,833	337

Infrared and ultraviolet spectra of [Mn (PyDCH) $_3$], PyH [Mn (DPA) $_2$] and [Mn (PyDCH) (PyDC) (H $_2$ O)] show the presence of ligands in complexes. In all cases, there are two absorption bands in the visible region. The presence of these two bands in [Mn (PyDCH) $_3$] complex indicates a lowering of the symmetry due to Jahn-Teller distortion. The presence of these two bands in PyH [Mn (DPA) $_2$] and [Mn (PyDCH) (PyDC) (H $_2$ O)] just indicates a lowering of the symmetry, but it is so difficult to say

due to Jahn-Teller distortion.

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