

(I) 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

An excellent example of a d^4 species undergoing Jahn-Teller distortion is Mn (III). 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, 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. 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.

It is interesting to consider β -manganese (III) acetylacetonate, $Mn(acac)_3$, which crystallizes with the space group $P2_1/c$. The structure reported by Morosin and Brathovde (MB) was believed to show no Jahn-Teller distortion [3]. However, the structure of $Co(acac)_3$ determined by Hon and Pfluger was found to be nearly identical to that reported by MB for Mn

$(acac)_3$ [4]. Since the possibility was strong that $Mn(acac)_3$ and $Co(acac)_3$ compounds were mislabeled, Fackler and Avdeef reexamined the structure of $Mn(acac)_3$ and suggested that the $Mn(acac)_3$ structure reported previously by MB was actually that of $Co(acac)_3$ [5]. Fackler and Avdeef found two short Mn-O average bond distances of 1.95 Å. and four long Mn-O bond distances averaging 2.00 Å. The β form of $Mn(acac)_3$ was reexamined by Stults et al., and their results are somewhat more precise [6].

Indeed, there are a significant number of structures reported for manganese (III) complexes which purport to demonstrate the existence of an axial distortion. However, in the majority of instances, the complexes investigated contain multifunctional ligands, in which case there are inherent constraints imposed upon the nature and extent of the distortion permitted. No X-ray data are reported for mononuclear manganese (III) complexes containing only identical, monofunctional ligands. Only in such a system can one expect to observe the full extent of a structural distortion and the attendant large spectral splitting. A suitable candidate for this study was found in the complex $Mn-(Urea)_6(ClO_4)_3$, which has been used over a period of years as a reagent in the synthesis of a variety of manganese (III) complexes. The hexaureamanganese (III) complex is reasonably stable in the absence of moisture, it does not seem to be subject to photodecomposition, and it is easily prepared. On the basis of solution, diffuse

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reflectance, and mull spectra data, this complex seems to be typically distorted. We have recently synthesized Bis (2, 2', 2''- terpyridine) manganese (III) perchlorate and Tris (Picolinato) manganese (III) monohydrate in this work.

Experimental Section

A) Preparation

1) Preparation of $[Mn(Urea)_6](ClO_4)_3$

As shown in a previous paper [7] crystals of the composition $[Mn(Urea)_6](ClO_4)_3$ can be easily obtained. We have used this complex as a reagent in the synthesis of a variety manganese (III) complexes.

2) Preparation of $[Mn(Terpy)_2](ClO_4)_3$

0.10 g (4.3×10^{-4} mol) 2, 2', 2''- Terpyridine was dissolved in 8 ml absolute ethanol. To this solution was added 0.14 g (2.0×10^{-4} mol) hexakis (urea) manganese (III) perchlorate. The mixture was stirred for 60 min. A dark green microcrystalline solid formed and was separated by filtration, washed with absolute ethanol, and placed in a dessicator over $CaCl_2$. Anal. Cald. for $[Mn(Terpy)_2](ClO_4)_3$: C, 43.95; N, 10.25; O, 23.41; Mn, 6.70. Found: C, 42.81; N, 11.29; O, 23.33; Mn, 6.1. Therefore, this ligand acts as a tridentate ligand.

3) Preparation of $[Mn(Pic)_3] \cdot H_2O$

0.37 g (3×10^{-3} mol) Picolinic acid was dissolved in 40 ml absolute ethanol. To this solution was added 0.71 g (1×10^{-3} mol) hexakis (urea) manganese (III) perchlorate. The mixture was stirred for 30 min. A red microcrystalline solid formed and was separated by filtration, washed with absolute ethanol, and placed in a dessicator over $CaCl_2$. Anal. Cald. for $[Mn(Pic)_3] \cdot H_2O$: H, 3.2; N, 9.65; O, 25.5; Mn, 11.9. Found: H, 2.82; N, 8.25; O, 27.5; Mn, 11.9. Therefore, this ligand acts as a bidentate ligand.

B) Infrared Spectra

In the IR spectrum of the $[Mn(Urea)_6](ClO_4)_3$ complex, two bands at 3370 and 3460 cm^{-1} are assignable to stretching vibrations of NH_2 group, are present. A broad band at 1650 cm^{-1} is assignable to the stretching vibration of carbonyl group and bending vibration of NH_2 group. The CO (1725 cm^{-1}) stretching frequency of free CO is lowered to 1650 cm^{-1} in its complex, also three bands at 1480, 1535, and 1580 cm^{-1} are assignable to C-N group, showing the C-N bond is stronger than the C-N bond in free urea. Therefore, urea molecule is coordinated through oxygen. Three bands at 1100, 625, and 940 cm^{-1} are assignable to the perchlorate group [8]. One band at 430 cm^{-1} could be assigned to the stretching vibration of Mn-O bond.

In the IR spectrum of $[Mn(Terpy)_2](ClO_4)_3$, the C-H stretching frequency appears at 3035 cm^{-1} . The presence of some bands in the 1600-1430 cm^{-1} region could be assigned to C=C and C=N stretching vibrations. Two bands at 760 and 650 cm^{-1} are assignable to the out of plane bending vibration of the C-H group. Also one weak band at 915 cm^{-1} is assignable to the perchlorate group [8]. One band at 415 cm^{-1} could be assigned to the stretching vibration of Mn-N bond.

In the IR spectrum of $[Mn(Pic)_3] \cdot H_2O$ complex, two bands at 3420 and 3080 cm^{-1} are assignable to stretching vibrations of OH group and C-H (ring) respectively. The carbonyl stretching frequency at 1675 cm^{-1} , showing $C \leftarrow O \rightarrow M$ configuration. The C-O stretching vibration appears at 1320 cm^{-1} . Three bands at 1440, 1460, and 1600 cm^{-1} are assignable to stretching vibrations of C=C and C=N. The out of plane bending vibrations of the C-H group appear at 710 and 750 cm^{-1} . Also two bands at 470 and 430 cm^{-1} could be assigned to Mn-N and Mn-O stretching vibrations, respectively.

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 indicate lowering of the symmetry due to Jahn-Teller distortion.

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

Chemical Formula	cm^{-1}	ϵ (lit mole $^{-1}cm^{-1}$)
$[Mn(Urea)_6](ClO_4)_3$	48,309	2,843
	38,462	2,143
	29,412	1,157
$[Mn(Terpy)_2](ClO_4)_3$	43,859	44,262
	36,630	33,196
	35,714	32,786
	32,258	22,131
$[Mn(Pic)_3] \cdot H_2O$	21,900	13,191

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

Chemical Formula	cm^{-1}	ϵ (lit mole $^{-1}cm^{-1}$)
$[Mn(Urea)_6](ClO_4)_3$	13,888	72
	19,600	179
$[Mn(Terpy)_2](ClO_4)_3$	18,348	106
	21,176	192
$[Mn(Pic)_3] \cdot H_2O$	19,230	143
	24,271	395

Conclusion

As we have mentioned before, an excellent example of a highspin d^4 species undergoing Jahn- Teller distortion is Mn (III). Considering the effective symmetry in a chelate system such as $M(AA)_3$ or $M(AB)_3$ in solution which is actually the same as an MX_6 system, i.e., O_h symmetry, only one spin allowed absorption band (${}^5E_g \rightarrow {}^5T_{2g}$) is to be expected in the approximately visible region. On the basis of Jahn-Teller distortion, two or three absorption bands are to be expected.

Infrared spectrum of $[Mn(Urea)_6](ClO_4)_3$ shows that the urea molecule is coordinated through oxygen. Infrared and ultraviolet spectra of $[Mn(Terpy)_2](ClO_4)_3$ and $[Mn(Pic)_3] \cdot H_2O$ 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 three complexes indicate lowering of the symmetry due to Jahn- Teller distortion.

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