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## DISSYMMETRIC SYNTHESIS OF A BINUCLEAR MANGANESE(II) COMPLEX \*

NASIR AHMAD

*Department of Chemistry, University of Islamabad, Islamabad*

S. KIRSCHNER

*Department of Chemistry, Wayne State University, Detroit, U.S.A.*

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**Abstract.** Extremely high optical rotations are observed when an excess of base is added to a system containing tris(*o*-phenanthroline)manganese(II) or tris(2,2'-dipyridyl)manganese(II) chlorides and optically active organic acids (such as D- or L-malic acids or tartaric acids). The precipitated perchlorate of the resultant complex has the empirical formula  $\text{Mn}(\text{phen})_2(\text{OH})(\text{ClO}_4) \cdot \frac{1}{2}\text{H}_2\text{O}$  and 3.9 B.M. as its magnetic moment. Freshly precipitated complex is partially soluble in acetone and formamide and is found to be optically active. After drying, the perchlorate becomes insoluble in a large number of polar and nonpolar solvents. Dissymmetric synthesis of a binuclear manganese(II) complex with bridging hydroxo groups under the influence of the optically active organic ion is assumed to be responsible for the very high optical rotations observed.

The Pfeiffer effect has been under investigation since 1931.<sup>1</sup> It is the change in the optical rotation of a solution of an optically active organic ion upon the addition of certain racemic metal complexes. Generally tris complexes of various metal ions like  $\text{Co}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$  and  $\text{Cd}^{++}$  with *o*-phenanthroline and 2,2'-bipyridine type ligands exhibit this effect.<sup>2,3</sup> In recent years various aspects of this effect have been studied and some very interesting results published.<sup>4-7</sup> We have already communicated<sup>8,9</sup> that a few less labile metal complexes can be obtained in optically active form after removing either the optically active organic ion or the metal complex from the system. Most of these studies indicated that a slight excess of *dextro* or *levo* enantiomer of the racemic complex is produced under the influence of active organic ion. This is rather a confirmation of the assumption made by Pfeiffer (discoverer of this effect) about the nature of this effect.

It was observed by Pfeiffer that the optical rotation of a solution of ammonium D-10-camphorsulphonate was appreciably decreased in the presence of  $[\text{Mn}(\text{phen})_3]^{++}$  ion.<sup>2</sup> While reexamining the effect in this complex with L-malic acid, quite an unusual behaviour was observed. A system containing tris(phenanthroline)manganese(II) chloride and L-malic acid exhibited the usual changes in optical rotations characteristic of the 'Pfeiffer effect.' However, when the system was made basic by adding aqueous ammonia or sodium hydroxide, a 25-30 fold increase in optical rotation was observed. This phenomenon was also observed with 2,2'-bipyridyl complexes and

in the presence of other optically active acids such as D-malic acid, D- or L-tartaric acids. It was possible to precipitate out a yellow complex as the perchlorate from the solution. Elemental analysis, magnetic moment, low solubility of the perchlorate in a large number of polar and nonpolar solvents, and other properties have led to the conclusion that an asymmetric binuclear manganese(II) complex cation (with hydroxo bridges) is produced in solution, which exhibits tremendously high optical rotation. This is the first recorded instance of a binuclear manganese(II) complex synthesised and resolved into its optically active antipodes.

### Experimental

*o*-Phenanthroline and 2,2'-bipyridine were obtained from G.F. Smith & Co. and used without further purification. Other compounds used were of reagent grade.

The optical rotations were measured on a Perkin-Elmer model 141 polarimeter. This polarimeter is equipped with mercury and sodium vapour lamps and suitable filters which can isolate five wavelengths: 589, 578, 546, 436 and 365 nm. The angles of rotation were measured using one decimeter-tube at sodium D line (589 nm) and at room temperature (22°C). The optical rotatory dispersion spectrum was determined with a Cary model 60 spectropolarimeter. Magnetic moments of the solid compounds were determined on a Guoy magnetic balance using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a standard.

Calculated amounts of the ligand were dissolved in aqueous solutions of metal salt and optically active organic acid by stirring and making up to the volume in a measuring flask. Concentration used were 0.02 molar with respect to metal complex and

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0.02–0.04 molar with respect to resolving agents. The bases used for polarimetric titrations were 50 times more concentrated than the metal complexes so that negligible changes of volume were produced.

It was observed that a yellow precipitate of  $[\text{Mn}(\text{phen})_2\text{Cl}_2]$  is produced when the mixture of *o*-phenanthroline and hydrated manganese chloride or sulphate (3:1 molar ratio) is stirred in water. A careful dissolution of the required quantities of the ligand in an aqueous solution of the metal salt and L-malic acid produced a yellow solution which exhibited the expected changes in optical rotation. However, prolonged stirring of the solution produced a yellow precipitate as before. The addition of an excess of a strong acid destroyed the complex, while slow addition of aqueous ammonia with constant stirring produced a slightly deeper yellow complex in solution. When checked, the optical rotation of the solution was found to be extremely high. Solution was prepared by slow stirring of the mixture containing ligand, hydrated manganese chloride and L-malic acid in proper proportions and was titrated with a concentrated solution of ammonia or sodium hydroxide and checking the optical rotation after each addition. Relatively small rotational changes were observed during the addition of first two mole-equivalents of the base while further addition produced very high rotations ranging from 5.0 to 6.0° as observed in one decimeter-tube.

### Results

A typical polarimetric titration with sodium hydroxide is shown in Table 1. The changes in optical rotation due to the added bases at different pH values are presented in Fig. 1.

Addition of more than 2.48 mole-equivalents of sodium hydroxide produced a precipitate of hydrated manganese oxide. Similar high rotations were observed in the presence of other optically active environment substances and manganese(II) complexes. Tris(2,2'-bipyridyl)manganese(II) chloride exhibited an ana-

TABLE 1. TITRATION OF THE SYSTEM  $[\text{Mn}(\text{phen})_3]\text{Cl}_2(0.02\text{ M})$ –L-MALIC ACID (0.02 M) WITH SODIUM HYDROXIDE.

NaOH (M)	Max. observed rotation (degrees)
L-Malic acid	0.003
0	— 0.198
0.002	— 0.210
0.004	— 0.223
0.008	— 0.245
0.012	— 0.258
0.020	— 0.285
0.030	— 0.304
0.040	— 0.439
0.042	— 1.754
0.044	— 3.502
0.046	— 4.905
0.048	— 6.440
0.050	Brown precipitate

logous behaviour. The systems producing high rotations are listed in Table 2.

The exaltation of optical rotations in these systems is reversible, i.e. the complex is destroyed by acidifying the solution and optical rotations are solely due to the asymmetric organic acid, whereas the yellow complex with very high optical rotations is formed upon the addition of a base.

It was considered necessary to determine the optimum conditions for observing the maximum optical rotations. The effect of increasing the amount of ligand in the system is shown in Fig. 2(A) whereas Fig. 2(B) illustrates the changes observed by increasing the amount of L-malic acid in the system. It is apparent that the maximum rotation is observed in the presence of three moles of *o*-phenanthroline for each mole of manganese(II) salt and the optically active organic compound. Similarly maximum optical rotation is achieved in the presence of 2 moles of L-malic acid for each mole of metal complex of the composition  $[\text{Mn}(\text{phen})_3]\text{Cl}_2$ .

The resultant complex after titration with a base can be precipitated with perchlorate ion. From measurements of the optical activity it is found that 97% of the asymmetric acid remains in the filtrate. The freshly precipitated, wet complex is partially soluble in acetone and formamide. These solutions were found to be optically active and racemize rapidly. After a short interval, the solutions of optically active metal complex in acetone became turbid and difficult to measure the rotations. A quick optical rotatory dispersion spectrum of the acetone solution of the precipitated metal complex, produced a plain curve (Fig 3).

However, after drying the yellow precipitated complex, it was found to be insoluble in most of the polar and nonpolar solvents. The precipitated per-

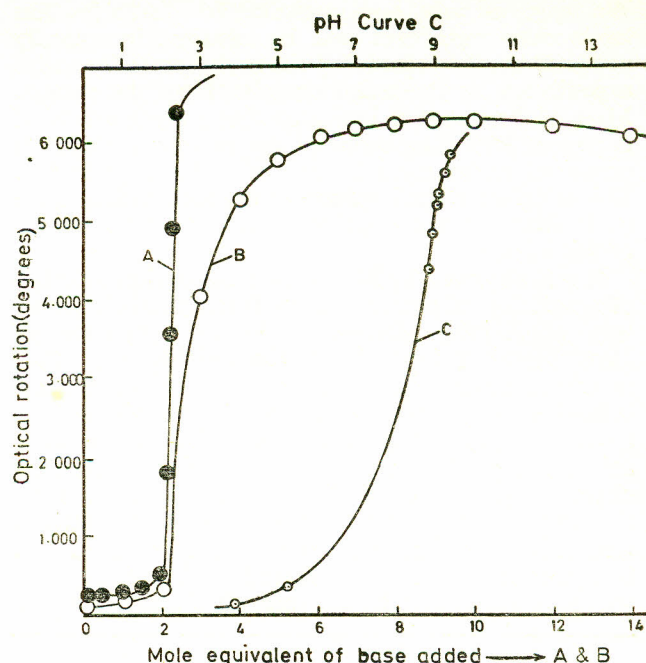


Fig. 1. Polarimetric titration of  $[\text{Mn}(\text{phen})_3]^{++}(0.22\text{ M})$ , L-malic acid (0.02 M) with (a) sodium hydroxide (b) ammonia (c) at different pH values.

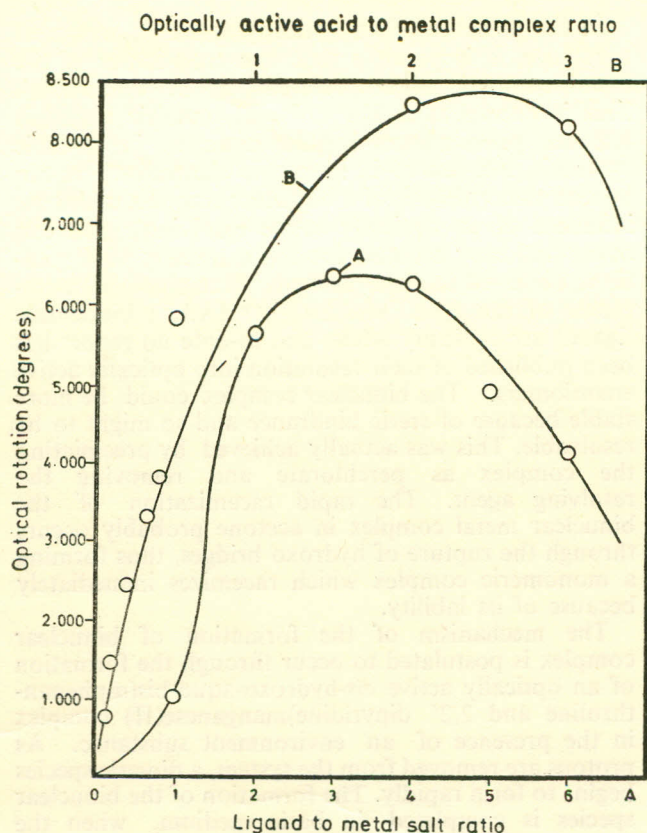


Fig. 2. Maximum optical rotations observed in the system containing  $MnCl_2$ , *o*-phenanthroline and L-malic acid. (A) By varying metal salt to ligand ratio, (B) by changing tris-metal complex to resolving agent ratio.

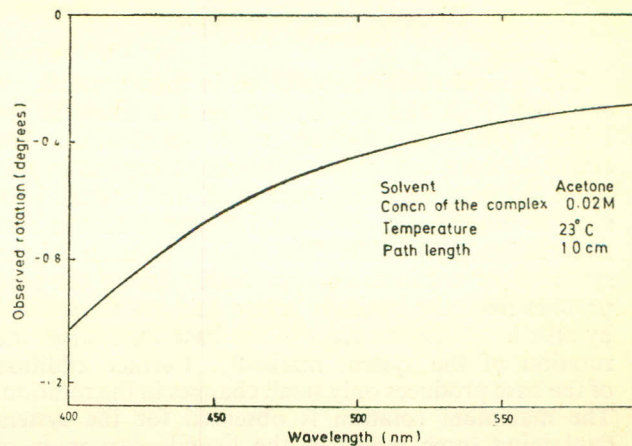


Fig. 3. Optical rotary dispersion spectrum of  $L-[Mn_2(phen)_4-(OH)_2](ClO_4)_2 \cdot H_2O$ .

chlorate was dried and analyzed for individual the elements. The results were computer-analysed for empirical formula determination and the possible formulae fitting the analysis were obtained as shown in Table 3.

The chemical analysis (C, 52.94; H, 3.34; N, 10.28; O, 16.78; Cl, 6.94 and Mn, 9.72%) of the precipitated perchlorate salt best fits the formula,  $[Mn_2(phen)_4-(OH)_2](ClO_4)_2 \cdot H_2O$  which is a binuclear compound. The magnetic moment of the solid substance was found to be 3.9 B.M. per manganese atom, which is substantially less than the expected value of 5.9 B.M. for a high spin manganese(II) ion.

TABLE 2. SYSTEMS EXHIBITING HIGH OPTICAL ROTATIONS.

System	Optically active organic acid	Optical rotation of the asymmetric acid $\alpha_e$ (degrees)	Pfeiffer rotation $P_{obs} = \pm(\alpha_e + c - \alpha_e)$ (degrees)	Titration agent	Max. observed rotation <sup>a</sup> (degrees) $\alpha_{max}$
$[Mn(phen)_3]^{++}(0.02)^b$	L-Malic (0.02) <sup>b</sup>	-0.003	+0.195	$NH_4OH$	-6.095
$[Mn(phen)_3]^{++}(0.02)$	L-Malic (0.02)	-0.003	+0.195	NaOH	-6.440
$[Mn(phen)_3]^{++}(0.02)$	D-Malic (0.02)	+0.003	+0.188	"	+5.168
$[Mn(phen)_3]^{++}(0.02)$	D-Tartaric (0.02)	+0.052	+0.418	$NH_4OH$	-2.209
$[Mn(phen)_3]^{++}(0.02)$	D-Tartaric (0.02)	+0.052	+0.418	NaOH	-3.765
$[Mn(phen)_3]^{++}(0.02)$	L-Tartaric (0.02)	-0.056	+0.398	NH OH	+3.154
$[Mn(dipy)_3]^{++}(0.02)$	L-Malic (0.02)	-0.003	+0.021	"	-1.171

<sup>a</sup>Optical rotation in a 1 dm-tube at 589 nm and 23°C; <sup>b</sup>molar concentrations.

TABLE 3. CHEMICAL COMPOSITION OF THE POSSIBLE METAL COMPLEXES.

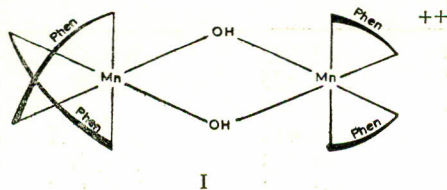
Compound	Mol. wt.	Calculated percentage composition				
		C	H	N	O	Cl
$[Mn(phen)_3](ClO_4)_2$	794.54	54.42	3.04	10.58	16.11	8.92
$[Mn(phen)_3](OH)(ClO_4)$	712.08	60.71	3.54	11.80	20.22	4.98
$[Mn(phen)_2](ClO_4)_2$	614.27	46.63	2.61	9.94	20.23	11.73
$[Mn_2(phen)_4(OH)_2](ClO_4)_2 \cdot H_2O$	1081.70	53.29	3.35	10.34	16.30	6.56
$[Mn_2(phen)_4(mal)](ClO_4)_2$	1161.71	53.75	3.12	9.64	17.90	6.10
$(Mn_2(phen)_5(mal))(ClO_4)_2$	1341.94	57.29	3.31	10.44	15.50	5.28

mal, malate anion.

### Discussion and Conclusions

The optical rotations observed in these systems are extremely high and could not be due solely to the Pfeiffer effect—a relatively weak interaction. The extent of these high rotations seems to depend in part upon the strength of the base used, and a weak base such as ammonia is less effective than a strong base like sodium hydroxide. The optical rotation of the system does not increase appreciably during the time protons from the optically active acid are neutralized by alkali. A slight excess of the base then raises the rotation of the system markedly. Further addition of the base produces only small changes in the rotation. The maximum rotation is observed for the system containing three moles of the ligand—one mole of the metal ion and two moles of the organic acid. These rotations are slightly decreased when the ratio of the metal complex to resolving agent is decreased to 1:1 or 2:1. These observations seem to indicate that there is not enough resolving agent to coordinate with the metal ion. The observation that the filtrate contains most of the resolving agent (after removal of the metal complex as a sparingly soluble perchlorate) further strengthens the postulate that the resolving agent does not enter the coordination sphere.

If the resolving agent is not in the coordination sphere, then there are only a few reasonable explanations for these unusually high rotations. A first order asymmetric synthesis could certainly be responsible for these rotations. The formation of a simple optically active complex such as D-(or L-[Mn(phen)<sub>3</sub>]-ClO<sub>4</sub>)<sub>2</sub> is not supported by elemental analysis of the precipitated complex. Moreover, this ion is extremely labile, and it has not yet been isolated in an optically active form. The empirical formula determined from the elemental analysis can be represented by [Mn(phen)<sub>2</sub>(OH)](ClO<sub>4</sub>)<sub>1.5</sub>H<sub>2</sub>O, which fits a binuclear complex very well. Thus a dimeric complex with hydroxo bridges such as shown below, is postulated as being synthesised in the basic medium.

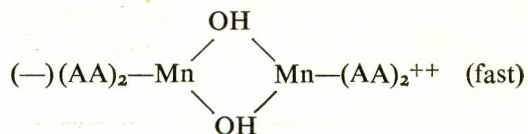
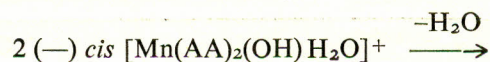
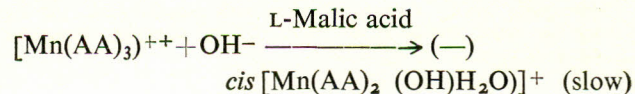


The relatively low value of the magnetic moment is also indicative of some metal-metal interaction in the form of a binuclear metal complex.

Binuclear complexes of these ligands with Fe(III) and Cr(III) have already been prepared and are well characterized.<sup>10-12</sup> Also Mason and Wood<sup>13</sup> have actually resolved binuclear complexes of this type with chromium(III). A dimeric molecule of this type should form *meso*, *dextro*(+) and *levo*(-) isomers in the statistical ratio of 2:1:1. However, models indicate that the *meso*-isomer, if formed at all, would be grossly hindered sterically, whereas the *dextro* and *levo*-isomers are relatively free from steric constraints.

In the presence of an optically active environment substance, it is possible that one enantiomer of the metal complex might preferentially be synthesised. This is known as a first order asymmetric synthesis and the phenomenon is quite common in organic synthesis, but less so in inorganic chemistry.<sup>14</sup> It can be seen that synthesis of a binuclear complex under the influence of an optically active resolving agent can occur and may account for the extremely high rotations observed in these systems. Manganese(II) complexes of the type [Mn(AA)<sub>3</sub>]<sup>++</sup> (AA, a bidentate ligand) are optically labile, and to-date no report has been published of their resolution into optically active enantiomers. The binuclear complex could be more stable because of steric hindrance and so might be resolvable. This was actually achieved by precipitating the complex as perchlorate and removing the resolving agent. The rapid racemization of the binuclear metal complex in acetone probably occurs through the rupture of hydroxo bridges, thus forming a monomeric complex which racemizes immediately because of its lability.

The mechanism of the formation of binuclear complex is postulated to occur through the formation of an optically active *cis*-hydroxo-aquo-bis(*o*-phenanthroline and 2,2' dipyridine)manganese(II) complex in the presence of an environment substance. As protons are removed from the system, a dimeric species begins to form rapidly. The formation of the binuclear species is completed in basic medium, when the rotatoin achieves its maximum.



(AA, *o*-phenanthroline or 2,2'-bipyridine)

The formation of the *levo* enantiomer of the dimer in the presence of D-tartaric acid might be due to the different absolute configuration of the resolving agent.

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