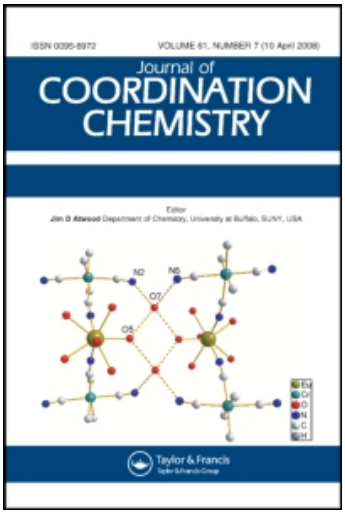

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation and Oxygenation of Manganese(II) Complexes of Imines Derived from Salicylaldehyde and Amino Acids

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To cite this Article Qing-Yu, He , Zhen-Hua, Mei and Ya-Mei, Zhang(1990) 'Preparation and Oxygenation of Manganese(II) Complexes of Imines Derived from Salicylaldehyde and Amino Acids', Journal of Coordination Chemistry, 21: 3, 199 — 207
To link to this Article: DOI: 10.1080/00958979009409716
URL: http://dx.doi.org/10.1080/00958979009409716

J. Coord. Chem. 1990, Vol. 21, pp. 199–207
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PREPARATION AND OXYGENATION OF MANGANESE(II) COMPLEXES OF IMINES DERIVED FROM SALICYLALDEHYDE AND AMINO ACIDS

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(Received April 7, 1989; in final form November 9, 1989)

Manganese(II) complexes of imines derived from salicylaldehyde and glycine, alanine, valine, phenylalanine and histidine were prepared and identified. Most of these compounds were found to be stable towards dry air but absorbed oxygen readily in many organic media to the extent of O_2/Mn equal to 1 or 0.5. Reversibility was barely observed except for complexes derived from valine and phenylalanine. The histidine analogue showed no reversibility.

Keywords: Manganese, Schiff bases, oxygenation, complexes

INTRODUCTION

The study of the formation of dioxygen adducts of coordination compounds of the first transition metal(II) ions has long attracted the attention of inorganic chemists in that some of the reactions resemble biological processes and serve as models for the biological reactions involved. Casella *et al.* have synthesized[1-6] a group of coordination compounds of Cu(II), Cu(I), Co(II), Ni(II), Zn(II) and Fe(III) with imines formed by the condensation of salicylaldehyde (sal), pyridoxal (pdx) or pyruvic acid (pyv) with *L*-amino acids (*L*-aa) and have observed that some members of the Co(sal-*L*-aa) and Co(pdx-*L*-aa) series bind dioxygen to the extent of Co/O_2 equal to 1 : 1 or 2 : 1.

With the view that some of these compounds, which bind oxygen reversibly under mild conditions, may serve as novel oxygen carriers or models for the study of oxygen transport or storage by respiratory proteins such as hemoglobin and myoglobin, the present authors have undertaken a synthesis of a series of Mn(II) complexes with imines derived from the condensation of salicylaldehyde and *L*-amino acids and a study of their behaviour towards oxygen. These compounds are designated Mn(sal-*L*-aa) where aa are the amino acids glycine (gly), alanine (ala), valine (val), phenylalanine (phe) and histidine (his). The amino acids were chosen to provide a comparison with the amino acids in the heme pocket of hemoglobin and myoglobin.

EXPERIMENTAL

Reagents

All amino acids were biochemical reagents, other chemicals being of analytical or equivalent grades. Purification before use was made when necessary.

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Mn(sal-L-aa), (aa = ala, val or phe).

These complexes were prepared by refluxing 5 mmol of the amino acids with an equal amount of salicylaldehyde in 50 cm^3 of degassed 3 : 1 ethanol/water under a nitrogen atmosphere for 2 hr. An equal number of millimoles of $Mn(Ac)_2.4H_2O$ was then added. For the preparation of Mn(sal-*L*-ala), continued reflux for about 1 hr was necessary, when a yellow precipitate began to separate. Further stirring for about 3–4 hr gave a large crop of yellow product. The precipitate was washed three times with small quantities of the above solvent, and dried in vacuum for at least 12 hr. A yellow powder was obtained as the final product (yield: 19%). For the preparation of Mn(sal-*L*-val) and Mn(sal-*L*-phe), cooling of the ligand reaction mixture to room temperature was necessary before addition of the Mn salt. Turbidity appeared about 10 min after the addition. The procedures then followed were the same as those above with final yields of 88% and 72% of the yellow, scaly solids Mn(sal-*L*-val) and Mn(sal-*L*-phe), respectively.

Mn(sal-L-his)

This complex was prepared by refluxing, in 30 cm^3 of degassed absolute alcohol, 5 mmol of *L*-his and an equal amount of salicylaldehyde under a nitrogen atmosphere for 10 min. A solution of 30 cm^3 of degassed absolute alcohol containing $Mn(Ac)_2.4H_2O$ in slight excess was then added dropwise, at a rate capable of maintaining uninterrupted reflux. Continuous reflux and stirring for 3–4 hr after addition of the manganese salt resulted in the separation of a large quantity of a yellow precipitate which was filtered and washed three times with small quantities of degassed 95% EtOH. The product was dried in vacuum for at least 12 hr. A 70% yield of yellow powder was finally obtained.

Mn(sal-gly)

5 mmol of glycine and a slight excess of salicylaldehyde were added to 50 cm^3 of 1:1 degassed EtOH/water. After 15 min reflux under nitrogen, a slight excess of $Mn(Ac)_2.4H_2O$ was added, and this dissolved immediately in the reaction mixture. Yellow turbidity appeared in 5 min. After aging for 1.5 hr, the reaction mixture was filtered and the precipitate washed three times with 50% EtOH, then dried in vacuum (yield: 90%).

Preparation of oxygenation products

Complexes prepared as outlined above were oxygenated in solution or suspension in a suitable medium as follows. A solution of 100 mg of complex in 25 cm^3 pyridine or formamide was stirred under dry air or 1 atm oxygen until the colour changed from yellow to brown and finally to brownish black. After complete absorption of oxygen, 50 cm^3 dry ether was added; this caused the separation of the oxygenated product as a brown precipitate, which was then filtered, washed three times with ether and finally dried in vacuum for seven days.

For oxygenation of a suspensoid, 100 mg of finely powdered complex was thoroughly dispersed in 25 cm^3 DMF or DMSO. The mixture was stirred under dry air or 1 atm oxygen until the colour became brownish black. The precipitate obtained was isolated in the same way as above.

Analysis

C and H were determined by Kobl's method, N by Kjeldahl's method and Mn by complexometric titration. Iodometry was employed for determination of peroxide.

Physical measurements

Measurements were made under nitrogen atmosphere whenever necessary. Ir spectra were obtained with a PE-683 spectrophotometer (4000–200 cm^{-1}) in KBr pellets and a NICOLET 5DX spectrophotometer (4000–400 cm^{-1}) in nujol mulls. Electronic spectra were recorded using a Shimadzu UV-260 spectrophotometer (800–190 nm) in dilute formamide or DMF solution. Tga was carried out with a Pct-1 system. X-ray studies were made on a modified Y-2a X-ray diffractometer. Oxygen uptake measurements were carried out in a modified Warburg system.

Deoxygenation and reversibility

Deoxygenation was effected by refluxing the oxygenated product under a nitrogen atmosphere in the same medium in which the original oxygenation took place. Noticeable change of the colour of the oxygenated product to its original form served as an indication of the reversal of the original process. The extent of reversal was determined by measuring the oxygen uptake of two successive oxygenation cycles under the same conditions. The percentage of the second oxygen uptake with reference to the first was defined as the percentage reversibility of the first oxygenation cycle.

RESULTS AND DISCUSSION

Synthesized Mn(II) compounds

Elemental analyses for the synthesized Mn(II) compounds are listed in Table I. Empirical formulae are derived from the analytical data. X-ray diffraction studies revealed that, in the products obtained, Mn does not exist as any of the species MnO_2, MnO, Mn_5O_8, Mn_3O_4, β-MnO_2 or Mn_2O_3.

TABLE I
Elemental analysis data for the synthesized Mn(II) compounds.

			C%	H%	N%	Mn%
1A	Mn(sal-gly).1/2H_2O	found:	44.37	3.41	5.52	
		calc'd:	44.83	3.34	5.81	22.79
2A	Mn(sal-*L*-ala).2H_2O	found:	42.96	4.68	5.17	19.55
		calc'd:	42.55	4.64	4.97	19.47
3A	Mn(sal-*L*-val).EtOH	found:	51.00	5.83	4.38	17.83
		calc'd:	50.99	5.60	4.58	17.94
4A	Mn(sal-*L*-phe).H_2O	found:	55.89	4.66	4.22	16.12
		calc'd:	56.46	4.44	4.12	16.15
5A	Mn(sal-*L*-his).EtOH.H_2O	found:	47.50	5.18	11.06	14.67
		calc'd:	47.88	5.09	11.17	14.60

Characteristic ir data for the Mn(II) compounds are listed in Table II. The absorption at about 1640 cm^{-1} indicates the formation of C=N,[1,2,3,6,8] which is common to all these compounds. The absorption at about 1545 cm^{-1} is characteristic of complexes derived from salicylaldehyde.[9] It originates from the coupling of the imino group to the benzene ring.

TABLE II

Electronic and ir spectral data for the synthesized Mn(II) compounds.

		λ_{max}nm(ε)*	Ir: (cm^{-1})
1A	Mn(sal-gly).1/2H_2O	359.6(4860)	1684s
		269.2(7110)	1543s
2A	Mn(sal-*L*-ala).2H_2O	358.6(5160)	1638s
		260.2(8620)	1537m
			1570s
3A	Mn(sal-*L*-val).EtOH	359.2(5240)	1644s
		269.4(9615)	1573s
			1540s
4A	Mn(sal-*L*-phe).H_2O	364.4(4310)	1640s
		267.6(9660)	1575s
			1542s
5A	Mn(sal-*L*-his).EtOH.H_2O	357.2(4500)	1635s
		266.0(7125)	1580s
			1564s

*Extinction coefficients: M^{-1} cm^{-1}.

Electronic spectral data for the synthesized Mn(II) compounds are also listed in Table II with Figure 1(a) given as a typical illustration. The two absorptions at about 360 nm and 266 nm as listed in the table originate respectively from $\pi \rightarrow \pi^*$ transitions of the imine[1,2,6] and the conjugation of the benzene ring coupled to it. Such general features indicate the formation of the salicylimine, in good agreement with the results of the ir studies.

Tga curves for all synthesized Mn(II) compounds take the form of Figure 2. With reference to the empirical formulae in Table I, assuming that the Mn(II) ion binds imine more strongly than a molecule of solvent, the weight loss marked by arrows in Figure 2, which is 3.82%, 12.22%, 14.99%, 5.94% and 17.01% for compounds 1A, 2A, 3A, 4A and 5A, respectively, may be rationalized as the result of elimination of the loosely bound solvent molecules. On this basis the theoretical weight loss of the various Mn(II) compounds is calculated to be 3.72%, 12.77%, 15.04%, 5.30% and 17.03%, respectively, in the above sequence. These agree fairly well with those experimentally found.

Oxygenation products

All the synthesized Mn(II) complexes, except for 4A which reacts slowly after 5 days exposure, are inert towards dry air but take up oxygen when dissolved or suspended in many organic solvents to the extent of 1 or 0.5 mol O_2 per mol of Mn. Data listed in Table III refer to an atmosphere of dry air, showing an increase of oxygen uptake

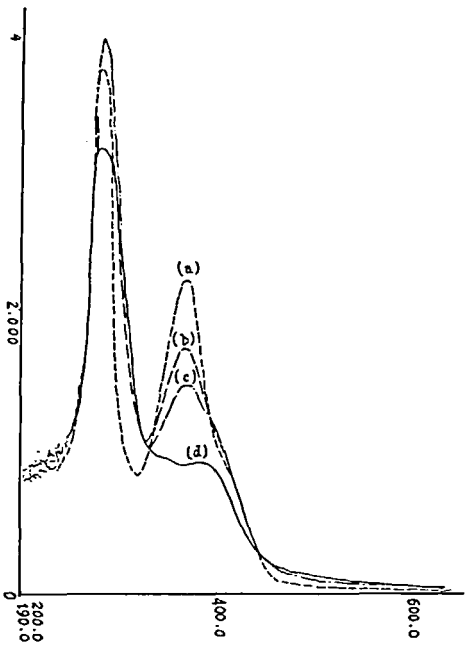

FIGURE 1 Electronic spectra for Mn(sal-*L*-val) in 2×10^{-4} M formamide (a) before oxygenation in nitrogen atmosphere; (b) 1.0 – 1.5 hr after oxygenation; (c) 4 hr after oxygenation; (d) 22 hr after oxygenation; (b)-(d) in 1 atm dry air.

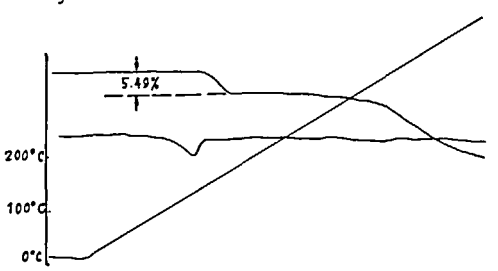

FIGURE 2 Tga for Mn (sal-*L*-phe) H_2O: 13.10 mg; 5°C/min; range 20–500°C; nitrogen atmosphere.

TABLE III
Extent of oxygen uptake of the Mn(II) complexes in various media (in terms of number of mols O_2 per mol Mn).

	py	DMF	Formamide	EtOH	MeOH	H_2O
1A	1					
2A	1	1	1	0.5		
3A	1	1		0.5	0.5	
4A	1	1	0.5	0.5		
5A	1	1	1			0.5

with increasing basicity of the medium. Results of elemental analysis of some of the oxygenation products together with empirical formulae derived therefrom are listed in Table IV. X-ray diffraction measurements of the complexes revealed no manganese oxides to be present.

TABLE IV

Analytical data and empirical formulae for some oxygenation products of the Mn(II) complexes.

			C%	H%	N%	Mn%
2B	Mn(sal-*L*-ala).py.O_2	found:	49.98	4.03	7.50	15.41
		calc'd:	50.44	3.95	7.84	15.38
3B	Mn(sal-*L*-val).py.O_2	found:	52.04	4.55	7.41	14.81
		calc'd:	51.77	4.34	7.55	14.80
4B	Mn(sal-*L*-phe).py.O_2	found:	58.81	4.77	6.73	12.58
		calc'd:	58.21	4.19	6.45	12.01
5B	Mn(sal-*L*-his).py.O_2	found:	51.57	3.94	13.11	13.09
		calc'd:	51.06	3.81	13.24	12.98

Characteristic ir spectra for the oxygenated Mn complexes are presented in Figure 3. The absorption at about 793 cm^{-1} owes its origin to the formation of O^{2-} [11,12] in the oxygenated Mn(II) complexes and that at about 627 cm^{-1} is due to Mn–O[12]. The reason for the lack of an absorption near 793 cm^{-1} for 2B is unknown. The νC=N stretch (about 1675 cm, not shown in Fig. 3) of the oxygenated products is somewhat shifted from that of the original complexes listed in Table II owing to the influence of the incorporated oxygen. The existence of O^{2-} is also confirmed by iodometry.

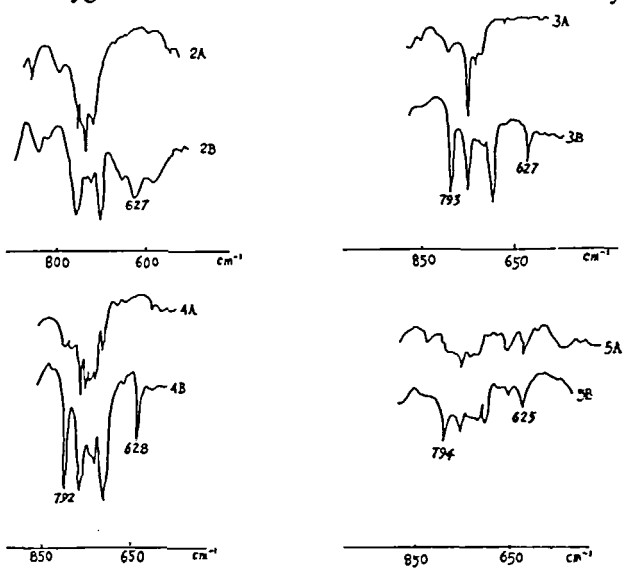

FIGURE 3 Ir spectra showing O_2^{2-} and Mn–O bonding in the oxygenated Mn complexes.

An illustration of the spectral changes upon oxygenation of the Mn(II) complexes is given in Figure 1. The skeleton structure of the original complex remains practically unchanged upon oxygenation and the weakening of the absorption near

360 nm and its final shift is rationalized as being a consequence of the influence of the incorporated oxygen on the central metal ion through which the C=N bond is ulitmately weakened.

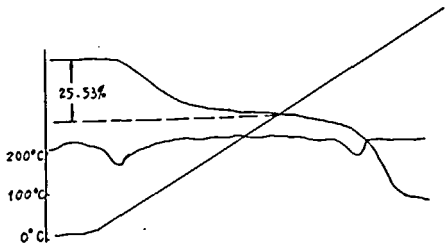

FIGURE 4 Tga for Mn(sal-*L*-phe).py.O_2: 16.20 mg; 5°C/min; range 25–600°C; nitrogen atm.

Tga for the oxygenated products is illustrated in Figure 4, the indicated weight loss being defined in exactly the same way as in Figure 2 with the Mn-imine linkage as a stable skeleton. The weight losses experimentally found are 30.51%, 30.89%, 25.53% and 25.92% for 2B, 3B, 4B and 5B, respectively, against calculated values of 31.09%, 29.92%, 25.63% and 26.24% in the same sequence. Results of tga support the idea that the Mn-imine fragment remains unchanged upon oxygenation. The resultant products probably take the form of a μ-peroxo polynuclear complex or a mononuclear chelate with bidentate O to conform to the rules of coordination number.

Reversibility of oxygenation of the Mn(II) complexes

Results of studies of reversibility of the oxygenation of the Mn(II) complexes are tabulated in Table V. It can be seen that only oxygenation in more basic media like py and DMF show reversibility. Further investigations on 3A in py and 4A in DMF are presented in Figure 5 and Figure 6.

TABLE V
Reversibility* of oxygenation of Mn(II) complexes in various media.

	py	DMF	Formamide	EtOH	MeOH
1A	40% (irr. after 3 cycles)		irr.	pract. irr.	pract. irr.
2A	20%	80% 2nd cyc. 20%	irr.	pract. irr.	pract. irr.
3A	60%	15%	irr.	pract. irr.	pract. irr.
4A	15%	60~70%	irr.	pract. irr.	pract. irr.
5A	irr.	irr.	irr.		

* % reversibility of the 1st oxygenation cycle.

In Figure 6 the resemblance between (C) and (A) in the neighbourhood of 267 and 364 nm indicates reversibility in the first oxygenation–deoxygenation cycle. However, the deviation of (C) from (A) as shown by the shoulder in the former suggests the formation of new species which complicates the system remarkably, resulting in the great deviation of (E) from (A) and the depression of oxygenation reversibility.

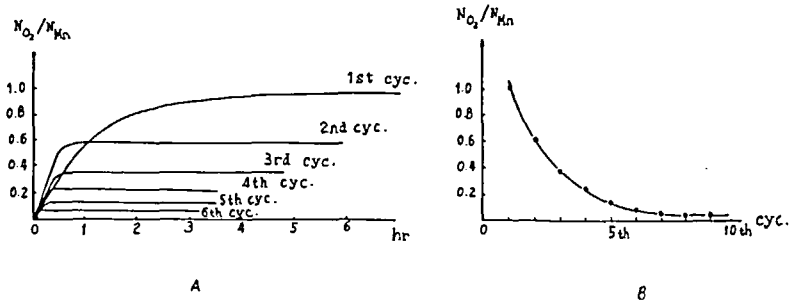

FIGURE 5 (A) Successive oxygenation curves for 3A in py;
(B) Decrease of oxygen uptake with repeated cycles of oxygenation.

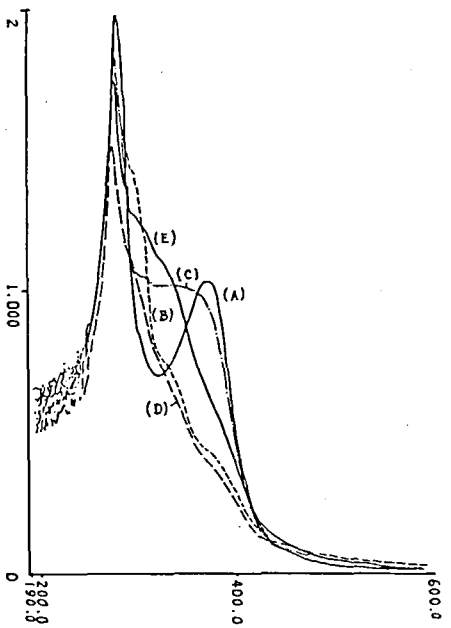

FIGURE 6 Electronic spectra showing reversible oxygenation of 4A in 2×10^{-4} M DMF;
(A) 4A before oxygenation;
(B) oxygenation product of 4A;
(C) deoxygenation product from (B);
(D) oxygenation product from (C);
(E) deoxygenation product from (D).

Figure 5 shows the results of the study of oxygenation reversibility by direct measurement of oxygen uptake. As a whole, the extent of reversibility of oxygenation of 3A in py is regularly and rapidly diminished as shown in the figure. However, Figure 5(A) depicts the emergence of a new species which takes up oxygen at a noticably greater rate than complex 3A, commencing from the 2nd cycle, and it appears that this new species plays an important role in following cycles.

The above experimental observations lead to the conclusion that reversible oxygenations are rare with the synthesized Mn(II) complexes, except for a few cases

in more basic media. Moreover, oxygenation–deoxygenation cycles involve very complicated reactions. It is rather interesting to note that compounds 3A and 4A containing valine and phenylalanine, which make contribution to the hydrophobicity of the heme pocket of hemoglobin and myoglobin, are the two compounds which show the greatest tendency of reversibility in binding oxygen, while compound 5A with histidine, which is also found in the heme pocket as the "distal histidine" but seems to make little contribution to hydrophobicity, shows no sign of reversible oxygenation.

ACKNOWLEDGEMENTS

We heartily thank Professor He Ren-jin for his help in preparing the figures.

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