BIVALENT METAL COMPLEXES OF SODIUM ASCORBATE

J. A. Obaleye* and C. L. Orjiekwe

Department of Chemistry, University of Ilorin, Ilorin, Kwara State, Nigeria

Abstract

The mode of coordination of manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), lead(II) and cadmium(II) to sodium ascorbate (NaHAsc) was investigated using IR, UV-visible, AAS, elemental microanalyzer, conductivity, magnetic and ^1H and ^{13}C NMR spectroscopic studies. NaHAsc is bidentate and coordination was through the carbonyl group and the oxygen atom of carbon-2 enolic hydroxyl group. The complexes are mainly high spin octahedral complexes based on the magnetic moment and spectral data.

Introduction

There have been few reports on the isolation of solid complexes of ascorbic acid despite numerous reports in the literature on the kinetics of its oxidation by metal ions [1-5]. Two basic conflicting reports on the mode of coordination of ascorbic acid to the metal ions have appeared [6, 7]. One group of investigators believed that ascorbic acid was chelated to the metal ions through the oxygen atoms on the C(2) and C(3) as shown in Figure 1 [1-4]. The other group of investigators isolated platinum(II) complexes of ascorbic acid of the type cis-[Pt (RNH$_2$) (ascorbate) and determined the structure using X-ray crystallography [5]. As expected, the ascorbate acted as a bidentate ligand. The surprising feature of the bonding was that it was not through the cis-oxygen atoms, but through C(2) and the oxygen atom attached to C(5) as shown in Figure 2. This appears to be the only unambiguous structure of ascorbic acid complex to be determined.

Apart from the reported cis-platinum(II) complexes, there is no other information in the literature on X-ray studies of other transition metal complexes of ascorbate

ions [5]. This may be the result of an inability to grow suitable crystals for X-ray studies.

In our previous investigations in this area [8-10], we reported the involvement of the carbonyl group and C(2) enolic hydroxyl group in complexation to the metal ion based on the IR and electronic spectra. Our report corroborates the fact that the monoascorbate species is the most predominant species in slightly alkaline media and carbon-2 enolic hydroxyl group is the more acidic group by virtue of its proximity to the carbonyl group [11].

In light of the foregoing, and in furtherance of our study in this area, we have attempted to reinvestigate the mode of coordination of ascorbate ions to some bivalent metal
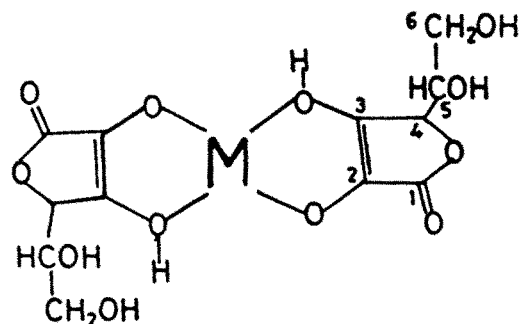
* To whom all correspondence should be addressed

Figure 1. Suggested structure for TiO_2^{+2}, Co^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{3+} etc. complexes of ascorbic acid

ions using sodium ascorbate. Several attempts have been made to grow crystals of the complexes in solvents (such as acetonitrile, methanol and dichloromethane) without any success in getting suitable samples for X-ray studies. The structures were established with the aid of spectroscopic techniques (IR, UV-vis., AAS, ^{1}H and ^{13}C NMR), correct elemental analysis, as well as chemical evidence.
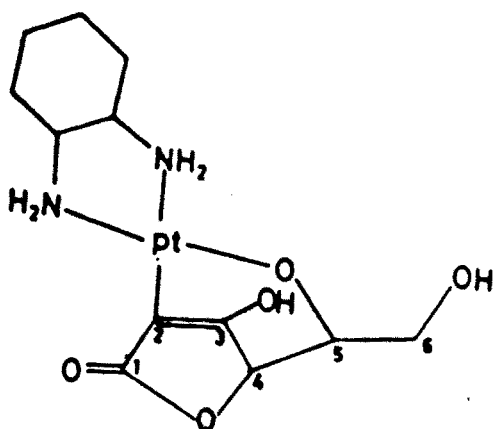

Figure 2. The *cis*-diaminecyclohexane platinum(II) complex of ascorbic acid

Materials and Methods

Materials

The sodium ascorbate and the metal salts were of analytical grade and were used directly, without further purification. The ethanol was dried in molecular sieves and purified according to standard methods.

Characterization Methods

The C, H and N contents were determined with an elemental analyzer at the Inorganic Laboratory, School of Chemistry, University of Bath, United Kingdom. The metal percentage was determined with a Unicam 360 MHz Atomic Absorption Spectrophotometer (AAS). The sodium percentage was obtained with a Unicam Flame Photometer using analytical grade NaCl for plotting the calibration curve. The infrared spectra were carried out in nujol mulls with a Unicam 360 MHz FT IR spectrophotometer using NaCl and CsI cells. The electronic spectra were recorded in MeOH with a Cecil series 6000 double beam spectrophotometer. The ^{1}H and ^{13}C NMR spectra were determined with a Joel JMN-GX 270 MHz FT NMR spectrometer and were recorded in DMSO using SiMe$_4$ as the internal standard. The magnetic susceptibility of the complexes was measured using the Gouy method and a Johnson-Matthey chemical balance. All other physical measurements and analytical procedures were similar to

those previously described in our earlier papers [8-10].

General Method for the Preparation of the Metal Complexes

Sodium ascorbate and the metal salts were measured in a 2:1 molar ratio into a 250 ml flask and refluxed in dry ethanol for about 8 hours under nitrogen. The mixture was filtered under nitrogen. The colored solid compound formed was recrystallized from dry ethanol and stored in CaCl$_2$ pellets contained in a dessicator.

Results and Discussion

The bivalent metal salts react with sodium ascorbate (NaHAsc) according to the general equations:

$$MX_2.6H_2O + 2NaHAsc \rightarrow M(NaAsc)_2.2H_2O + 2HX+4H_2O$$
where X=Cl.
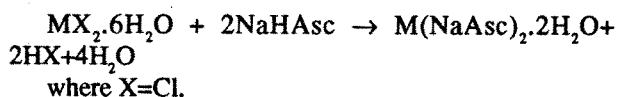
The physical properties and elemental analyses (Table 1) agree well with the formation of complexes. The evaluated empirical formulae indicate disubstitution of the ligand about the coordination sphere of the central metal ion. Six-coordinate geometries (octahedral) have been assigned for the complexes based on the values of magnetic moment and spectral results. The melting points of all the complexes are very high (>300°C).

The assignment of the vibration spectra (Table 2) has been carried out in accordance with our previous papers [8-10,12]. The characteristically weak and strong carbonyl stretch bands observed in the complexes are strongly distinct from those of ascorbic acid (H$_2$Asc) and NaHAsc and area strong indication of the involvement of the carbonyl group in chelate formation [13-15]. For example, in the case of Pb (NaAsc)$_2$.2H$_2$O spectrum, the C=O stretch band was observed at slightly lower frequencies relative to that in the spectrum of pure sodium ascorbate. This observation may be due to a reduction in the double bond character of C=O bands caused by complexation [9]. Apart from the C=O stretch band, the v_{c-o} band was influenced when compared to that of the free ligand after complexation. The presence of these two v_{co} absorption bands in the IR spectra data of the complexes may be due to the presence of two CO groups bonded to the same metal M with different CO... M band strengths[16]. The sodium ascorbate ring was not ruptured in the course of the complexation.

The electronic spectra of NaHAsc and the complexes are shown in Table 2. The bands at 260-269 nm in the free ligand and the complexes have been attributed to intra-ligand transition. The blue shift observed in the complexes relative to the free ligand have been attributed to complexation. The lower band at 203-208 nm, which is peculiar to the complexes, is assigned to a charge transfer

from L→M based on their ε max value and the fact that this band was present in cadmium(II), zinc(II) and lead(II) complexes which possess ^nS spectroscopic term symbol (where n=1 or 6). However, cobalt(II) and nickel(II) complexes gave additional bands which have been assigned to d→d transitions as expected. The bands at 320, 380 and 393 nm observed in copper(II), cobalt(II) and nickel(II) complexes respectively, have been assigned to the expected lowest transitions $^2T_2g→^2Eg$, $^4T_1g→^4T_2g$ and $^3A_2g→^3T_2g$ respectively, for the octahedral complexes in accordance with a previous st udy[8]. The higher transitions expected for cobalt(II) and nickel(II) complexes appear to have been submerged by the more intense charge transfer and intra-ligand transitions because of their relative intensities and proximity. In the manganese(II) complex the peak at 203-208 nm is of a relatively lower intensity than the 266 nm band. Consequently, the peak appears to have been submerged by the 266 nm band. As a matter of fact, the band at v266 nm is close to a value of 263 nm calculated using the rule for absorption of α, β- unsaturated ketones.

The NMR spectra (Table 3) of the diamagnetic complexes show appreciable chemical shifts only in ^{13}C NMR. These were observed in C(1) and C(2) for the metal complexes compared to the free ligand. It is expected that the bonding through C(1) leads to a decrease in the double bond character of the carbonyl group which results in an upfield chemical shift in the metal complexes. On the other hand bonding through the oxygen atom of the C(2) enolic hydroxyl group reduces its electronic influence on the ethylenenic double bond which results in a down field chemical shift.

The metal complexes are slightly soluble in water at room temperature which necessitated the determination of the Na content in dilute acetic acid. This property, coupled with the conductivity measurements obtained for the complexes, suggests a bidentate character for the ligand with coordination through the carbonyl group and carbon-2 enolic hydroxyl group. This is possible through ionization.

μeff. for Co (NaAsc)$_2$.2H$_2$O is above average as a result of considerable contribution from orbital angular momentum. The μeff. for the Co^{II} ion is usually higher than the spin only value since orbital contribution to the moment is observed for the ^4T_1g ground term [17]. It must be noted that weak antiferromagnetic interactions may lead to "normal" room temperature moments.

In view of the foregoing, the following multi-step mechanism has been proposed for the reaction of the metal ions with NaHAsc.

Table 1. Physical properties and elemental analyses of the ascorbate complexes

Compound	N	C	H	M%	Na%	Empirical Formula	μeff (B.M.)	Λ Ω^{-1} cm^{2}mol^{-1}
Mn[NaAsc]$_2$2H$_2$O	0.00 (0.0)	29.5 (29.57)	3.57 (36.69)	11.15 (11.30)	9.20 (9.44)	MnNa$_2$C$_{12}$H$_{16}$O$_{14}$	5.9	261.3
Co[NaAsc]$_2$4H$_2$O	0.00 (0.0)	27.25 (27.32)	4.01 (4.12)	10.9 (11.18)	8.45 (8.73)	CoNa$_2$C$_{12}$H$_{20}$O$_{16}$	6.2	259.6
Ni[NaAsc]$_2$4H$_2$O	0.0 (0.0)	27.20 (27.34)	4.11 (4.17)	9.47 (9.73)	8.4 (8.7)	NiNa$_2$C$_{12}$H$_{20}$O$_{16}$	2.88	260.4
Cu[NaAsc]$_2$2H$_2$O	0.0 (0.0)	28.8 (29.18)	3.10 (3.24)	12.67 (12.87)	9.10 (9.32)	CuNa$_2$C$_{12}$H$_{16}$O$_{14}$	1.8	260.1
Zn[NaAsc]$_2$2H$_2$O	0.0 (0.0)	28.7 (29.04)	3.15 (3.23)	13.08 (13.20)	9.15 (9.29)	ZnNa$_2$C$_{12}$H$_{16}$O$_{14}$	0.64	261.2
Pb[NaAsc]$_2$2H$_2$O	0.0 (0.0)	22.47 (22.53)	2.75 (2.81)	31.70 (32.50)	7.1 (7.22)	PbNa$_2$C$_{12}$H$_{16}$O$_{14}$	0.84	260.5
Cd[NaAsc]$_2$2H$_2$O	0.0 (0.0)	26.4 (26.57)	2.83 (2.95)	20.4 (20.66)	8.33 (8.48)	CdNa$_2$C$_{12}$H$_{16}$O$_{14}$	0.71	260.3

Values in parentheses are calculated values.

**Table 2ᵇ.** Selected infrared and electronic absorption spectra for characterization of the ascorbate complexes.

	Infrared bands (cm⁻¹)					Electronic bands (nm)
	V (O-H)	V(C=O)	δ (O-H)	V (C-O)	V (m-O)	
H_2Asc	3526s, 3412s, 3223s, 3032s, 2816s	1755s, 1674vs	1321s	1142s, 1120s, 1026vs		269 (4.5)
NaHAsc	3310s, 3250s	1703s, 1599vs	1363m, 1275s	1157m, 1051m		266 (4.39)
$Mn(NaAsc)_2.2H_2O$	3327s, br	1728w, 1601s	1315m	1151m, 1113m, 1041m	667w 459vs	267 (4.35)
$Co(NaAsc)_2.2H_2O$	3406s, br	1618vs	1359s	1153m	619w, sh 491m	203 (3.4) 266 (4.56) 380 (2.06)
$Ni(NaAsc)_2. 2H_2O$	3422s, br	1726w, 1612s	1383m	1219m, 1151m, 1111m	620m 489m	208 (3.5) 266 (4.51) 393 (2.2)
$Cu(NaAsc)_2.2H_2O$	3370s, br	1616s	1365m	1249m, 1049m	503m	205 (3.45) 260 (4.56) 320 (2.38)
$Zn(NaAsc)_2.2H_2O$	3429s, br	1720w, 1618s	1388m	1113m	721m	200 (3.46) 265 (4.54)
$Pb(NaAsc)_2.2H_2O$	3422s, br	1701w, 1591vs	1385vs	1145w	700m 489m	208 (3.5) 265 (4.49)
$Cd(NaAsc)_2.2H_2O$	3472s, br	1624s	1398m	1142m	721m	208 (3.56) 266 (4.50)

ᵇValues in parentheses are the absorptivity maxima ($^{\varepsilon}$max) in log 10.

Table 3ᶜ. ¹H and ¹³C NMR spectra of NaHAsc and its Cd(II) and Cu(II) complexes

	¹H NMR signal positions (δ) (ppm)				¹³C NMR signal positions (δ) (ppm)					
	C(g)-H	C(s)-H	C(6)-H	O-H	C(3)	C(2)	C(1)	C(4)	C(5)	C(6)
NaHAsc	4.99s	3.99t	3.72d	4.8s	174.96	173.28	110.67	76.07	67.25	60.25
$Cd(NaAsc)_2.2H_2O$	4.72s	4.0-4.05t	3.7-3.73d	4.8s	175.19	166.05	115	77.24	69.16	62.18
$Pb(NaAsc)_2.2H_2O$	4.71s	4.04-4.04t	3.7-3.72d	4.8s	175.0	165	115.2	77.3	69.2	62.3
$Zn(NaAsc)_2.2H_2O$	4.75s	4.1-4.04t	3.7-3.72d	4.8s	175.2	166.2	114.8	77.0	69.1	62.2

ᶜs = singlet, d = doublet, t = triplet, q = quartet, values in parentheses are integral values.
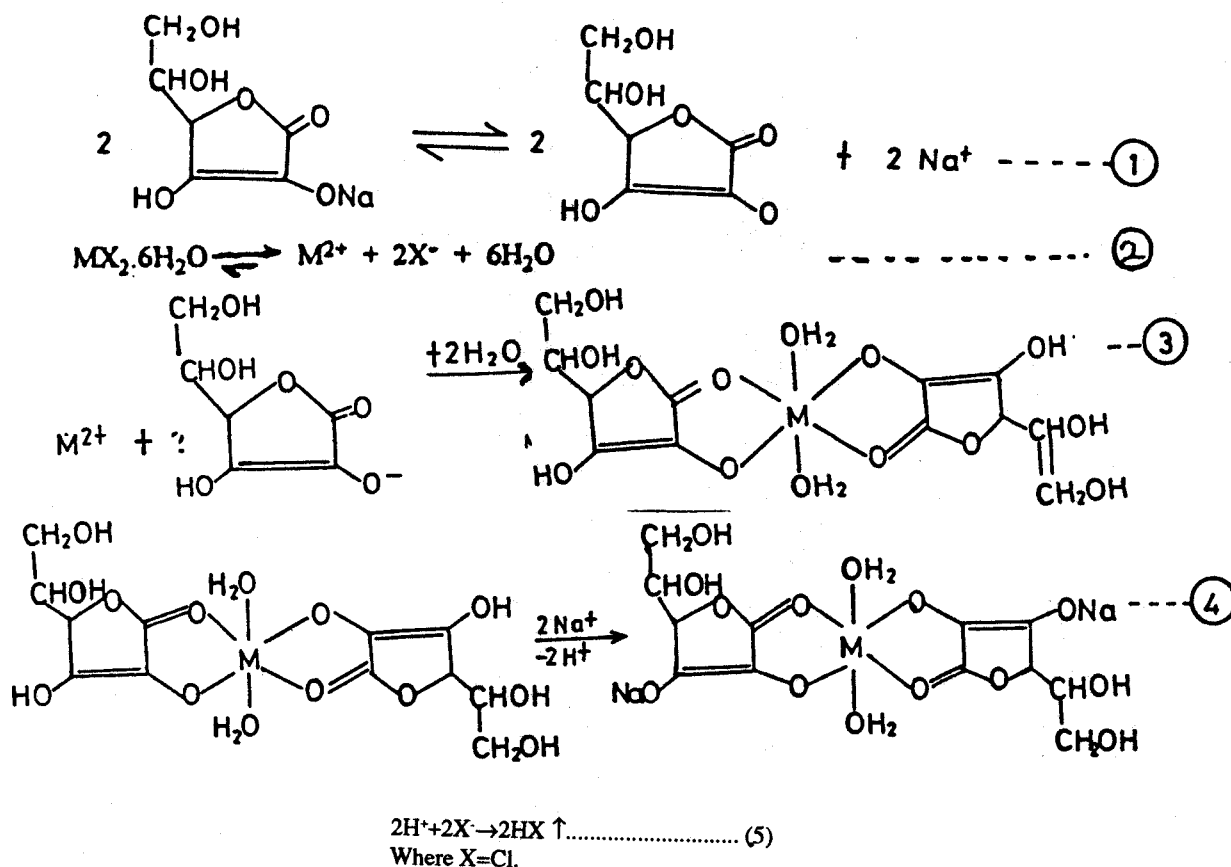
$$2H^+ + 2X^- \rightarrow 2HX \uparrow \quad\quad\quad (5)$$

Where X=Cl.

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