

A Joint Study on Juglone Metal Complexes by Infrared Spectroscopy and Density Functional Theory Calculations

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Abstract. Juglone is a natural product obtained from plants (e.g. walnut) showing bioactivities that were employed in past folk medicine and currently attracting interest for its cytotoxic effects. Complexes between juglone and Cu(II) or Ni(II) ions, whose stoichiometry was supported by ESI-MS experiments, were analyzed by FT-IR spectroscopy and the frequencies assigned by Density Functional Theory (DFT) calculation. The changes induced by metal chelation are discussed also in comparison with the ion-dipole interactions observed for Na and Cs salts of juglone.

Keywords: DFT calculations, IR Spectroscopy, Juglone, Metal complexes

Introduction

Juglone [=5-hydroxy-1,4-naphthalenedione, Scheme 1] is a natural product isolated from plants belonging to *Juglandaceae* genus (e.g. walnut). Past folk medicine used extract of walnut for antimicrobial, anti-inflammatory and antioxidant treatments. Recently Juglone has shown a cytotoxic activity on human tumour cells (HL-60, HL-60R, A549, SCG-7901) by inducing apoptosis.¹ Juglone metal complexes with Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) have shown antibacterial activity.²

Over the last decades, infrared spectroscopy has experienced a renewed role in the molecular structure elucidation of organic compounds, due to the availability of simulated spectra by density functional theory (DFT) calculations, used to assign the frequencies of chemical bonds through comparison with experimental data. From here our interest in the study by IR spectroscopy (through the comparison of experimental and simulated spectra) on Cu and Ni metal complexes, as well as on Na and Cs salts.

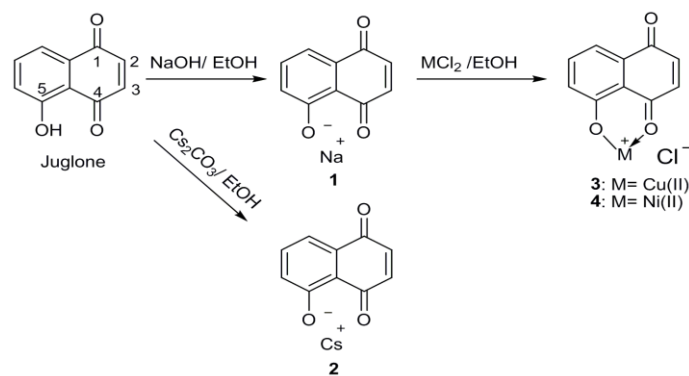
Experimental

IR spectra were recorded on solid samples by using the FTIR Bruker Equinox 55, fitted with an ATR crystal zinc selenide (ZnSe). Frequency values ± 1 cm⁻¹. DFT calculations were performed with Gaussian 03W, using B3LYP/6-311G(d) level of theory. The values of IR frequencies were scaled by a 0.96 factor.

The complex stoichiometry is supported by ESI(+)-MS data: **3:** m/z : 254 [M + H]⁺; **4:** m/z : 249 [M – H+H₂O]⁺

Results and Discussion

IR frequency assignments of the groups involved in each complex formation and in alkali salts (Scheme 1), were obtained by DFT calculated spectra (Figure 1 and 2) and are reported in Table 1.



Scheme 1: Preparation of Juglone salt and metal complexes

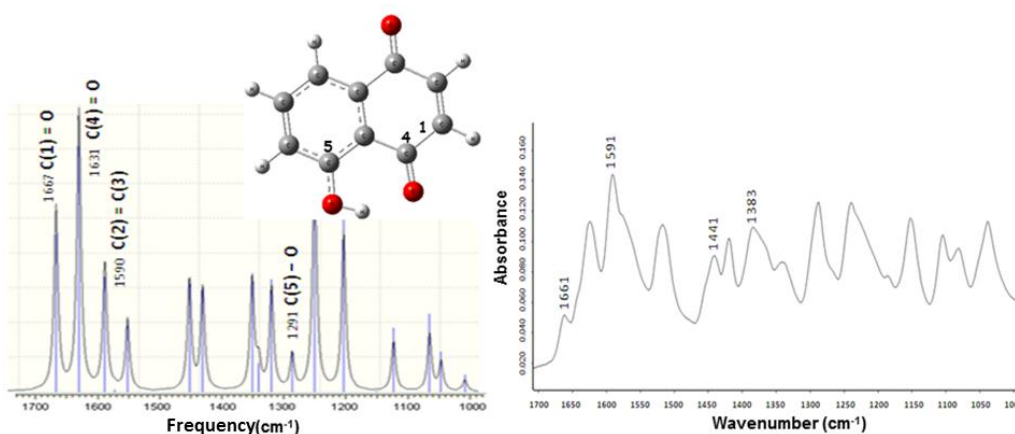


Figure 1. Region of interest in IR spectra for juglone: experimental (right) and DFT calculated (left) with assignments according to the numbering reported on the energy-minimized structure.

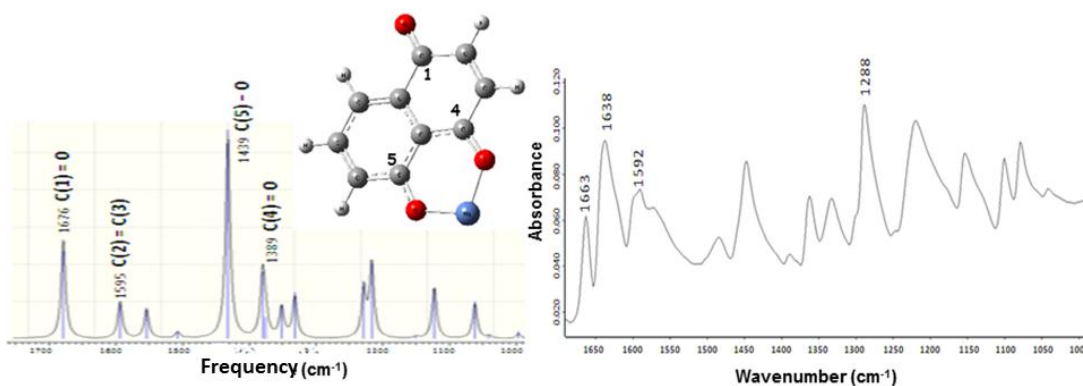


Figure 2. Region of interests in IR spectra for juglone-Ni(II) complex: experimental (right) and DFT calculated (left) with assignments according to the numbering reported on the energy-minimized structure.

Calculated frequencies for C(4)=O and C(5)-O⁻ groups in the free juglone anion are equivalent, due to the resonance involvement as shown in Figure 3.

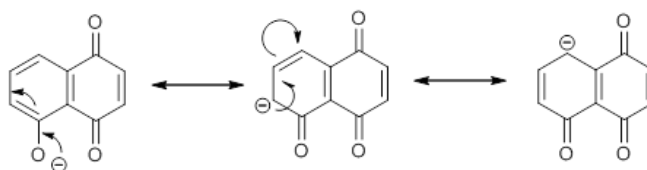


Figure 3. Resonance forms for Juglone anion.

Computed data for the structure regarding the alkali metal ion are in agreement with the experimental values. The frequency values of C(4)=O and C(5)-O⁻ groups in the salts are affected by the metal ion.

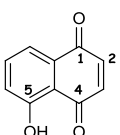
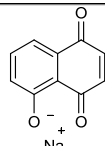
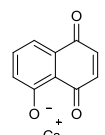
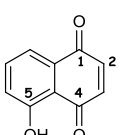
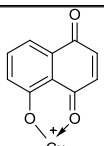
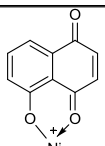
Table 1							
	v (cm ⁻¹)		v (cm ⁻¹)			v (cm ⁻¹)	
	Exp	Calcd	Exp	Calcd anion	Calcd salt	Exp	Calcd salt
C(1)=O	1663	1667	1660	1628	1653	1578	1542
C(4)=O	1638	1631	1574	1615	1553	1452	1484
C(2)=C(3)	1592	1590	1628	1628	1617	1612	1617
C(5)-O	1288	1291	1459	1615	1437	1417	1419

Table 2 reports data for Cu and Ni complexes. C(4)=O group actively participates to chelation and it shows a greater decrease in frequency value, corresponding to the partial loss of double bond character. C(5)-O group undergoes an increasing frequency value due to resonance stabilization and chelation.

Table 2						
	v (cm ⁻¹)		v (cm ⁻¹)		v (cm ⁻¹)	
	Exp	Calcd	Exp	Calcd	Exp	Calcd
C(1)=O	1663	1667	1655	1676	1661	1676
C(4)=O	1638	1631	1391	1383	1383	1389
C(2)=C(3)	1592	1590	1619	1600	1591	1595
C(5)-O	1288	1291	1424	1430	1441	1439

Conclusions

Although the comparison between experimental spectra recorded in the solid state and DFT calculated frequencies in gas phase, the relatively simplified model here proposed provides a good agreement for the group frequencies in the two systems. Significant variations were observed for the alkali salts with the only evidence for ion-dipole interactions, whereas the changes in Cu (II) and Ni(II) complexes are attributable to the involvement of chelation.

References

1. Polonik S. G., Prokof'eva N. G., Agafonova I. G., Uvarova N. I., *J. Pharm. Chem.*, **2003**, 37, 397-398.
2. Joshi C. R., *Indian J. Pharm. Sci.*, **1986**, 48, 101-104.