

## Short Communication

# Spectroscopic and Magnetic Properties of a Ni(II) Complex with Citric Acid

M. G. BOVI MITRE,<sup>1</sup> N. R. WIERNA,<sup>1</sup> C. C. WAGNER,<sup>2</sup>  
AND E. J. BARAN\*<sup>2</sup>

<sup>1</sup>*Cátedra de Química General e Inorgánica, Facultad de Ingeniería, Universidad Nacional de Jujuy, 4400 S. S. de Jujuy, Argentina; and* <sup>2</sup>*Centro de Química Inorgánica (CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C. Correo 962, 1900 La Plata, Argentina*

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## ABSTRACT

The complex compound  $K_2[Ni(cit)(H_2O)_2] \cdot 4H_2O$  (cit = triionized citrate ion) seems to be a good model for the investigation of Ni(II)/citrate interactions that are of interest in relation to nickel metabolism and bioaccumulation. Its infrared and Raman spectra were recorded and analyzed on the basis of its structural peculiarities. The magnetic susceptibility, investigated in the temperature range between 1.9 and 300 K, shows the absence of magnetic interactions between the two metal centers present in this structure.

**Index Entries:** Nickel; citrate; IR spectrum; Raman spectrum; magnetic susceptibility.

## INTRODUCTION

Although nickel was suggested as an essential nutrient more than 20 yr ago, conclusive definition of a biological function in the higher forms of life has been elusive (1-3). A great number of plants has been demonstrated to require nickel for growth (4,5) and it has also be shown

\*Author to whom all correspondence and reprint requests should be addressed.

that it is beneficial for different animals (6). A number of bacterial enzymes such as carbon monoxide dehydrogenase, different hydrogenases, some ureases and methyl-coenzyme-M-reductase are also nickel dependent (5,7,8).

The fact that many plants also contain urease explains, at least, some of the positive effects of nickel in plants. On the other hand, certain plants can accumulate very high concentrations of the element. Although they are usually known as "nickel hyperaccumulators," there is not concrete evidence for its essentiality in these plants (5).

Other studies indicate that signs of nickel deprivation in animals include depressed growth, reproductive performance and plasma glucose. It also affects the distribution and normal functioning of other nutrients, including calcium, iron, zinc, and vitamin B<sub>12</sub> (1–3).

Metabolic studies with higher animals show that most of the orally ingested nickel remains unabsorbed by the gastrointestinal tract and is excreted in the feces (5,6). Apparently, less than 10% of ingested nickel is absorbed. Its transport in blood is accomplished by serum albumin and by some amino acids. In addition, the above-mentioned effect of hyperaccumulation apparently involves Ni(II) complexes of relatively simple chelating agents, such as, malonic, malic, or citric acids (5).

As model studies related to nickel metabolism in the higher forms of life are relatively scarce, we have initiated some studies in this direction in order to attain a deeper insight into the general behavior and physico-chemical properties of bioinorganic systems relevant to this metabolic pattern.

As citrate has been shown to be a ligand for Ni(II) in plants and has also been suggested as a potential ligand for metal ions in plasma (9), we have now undertaken a study on the spectroscopic and magnetic properties of the 1:1 complex that Ni(II) forms with citric acid.

The stability constant of the 1:1 Ni(II)/citrate complex is in the same range as those for the most common bidentate amino acids (9). Notwithstanding, at the physiological pH value, the conditional stability constant of the citrate complex is 2.5 logarithmic units higher than those of the amino acids. On the basis of such an analysis, it has been suggested that a mixed histidine–citrate complex may constitute a significant fraction of plasma Ni(II) (9).

On the other hand, the increasing use of citric acid in foods and beverages generates additional interest on this ligand, especially in relation with its effect on trace metals uptake.

## MATERIALS AND METHODS

### *Synthesis of the Complex*

The complex, of composition  $K_2[Ni(C_6H_5O_7)(H_2O)_2]_2 \cdot 4H_2O$ , was prepared by the slow addition of 150 mL of a 1M KOH solution to 50 mL

of a 1M citric acid solution, with continuous stirring, followed by the addition of 50 mL of a 1M nickel chloride solution. The pH was adjusted to about 5.0 with further KOH, if necessary. After 1 wk, green crystals of the complex were obtained and its stoichiometry confirmed by elemental analysis (10).

### ***Physicochemical Measurements***

The infrared spectra, between 4000 and 200  $\text{cm}^{-1}$ , were obtained with a Perkin-Elmer 580 B spectrophotometer using the KBr pellet technique. Raman spectra of the powdered samples in glass capillaries were recorded on a Ranishaw Ramascope 2000 instrument, using the 514.5-nm line of an argon-ion laser for excitation.

Magnetic susceptibility measurements were made using a Quantum Design SQUID MPMS XL-5 magnetometer in the temperature range between 1.9 and 300 K. The equipment was calibrated with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  and metallic palladium. The magnetic field used was 100 Oe.

## **RESULTS AND DISCUSSION**

### ***Structural Characteristics***

The investigated complex,  $\text{K}_2[\text{Ni}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})_2]_2 \cdot 4\text{H}_2\text{O}$ , crystallizes in the triclinic space group  $P(-1)$  with  $Z = 1$ . It presents a centrosymmetric dimeric structure, with each triionized citrate ion bound as a tridentate ligand (through two carboxylate oxygens and the hydroxyl oxygen) to one Ni(II) ion, and providing a bridging bond to the second Ni(II) ion through the third carboxylate oxygen. Octahedral coordination of the metal centers is completed by two water molecules (10).

### ***Infrared and Raman Spectra***

The infrared (IR) and Raman spectra, in the range between 1800 and 250  $\text{cm}^{-1}$ , are shown in Figs. 1 and 2, respectively. The assignment of these spectra is complicated by the fact that vibrational modes of different origins appear superimposed in most of the spectral regions. Notwithstanding, in Table 1, we propose an assignment, based on general literature data (11,12) as well as on spectra of related species recently investigated in our laboratory (13,14). This assignment is briefly commented, as follows:

- The  $\nu(\text{O}-\text{H})$  stretching of the alcoholic group (not shown in the figures) is seen as a strong and well-defined IR band at 3511  $\text{cm}^{-1}$  and as a medium-intensity feature at 3508  $\text{cm}^{-1}$  in the Raman spectrum. Stretching vibrations of the water molecules (also not shown in the figures) generate medium-intensity bands (3447  $\text{cm}^{-1}$  in the IR and 3445  $\text{cm}^{-1}$  in the

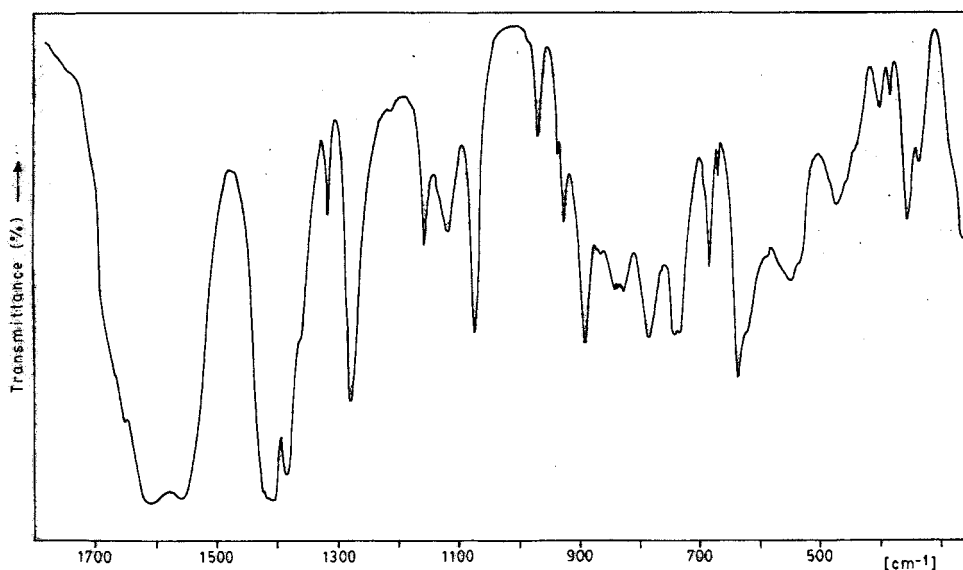


Fig. 1. Infrared spectrum of  $K_2[Ni(C_6H_5O_7)(H_2O)_2]_2 \cdot 4H_2O$  in the range between 1800 and 250  $cm^{-1}$ .

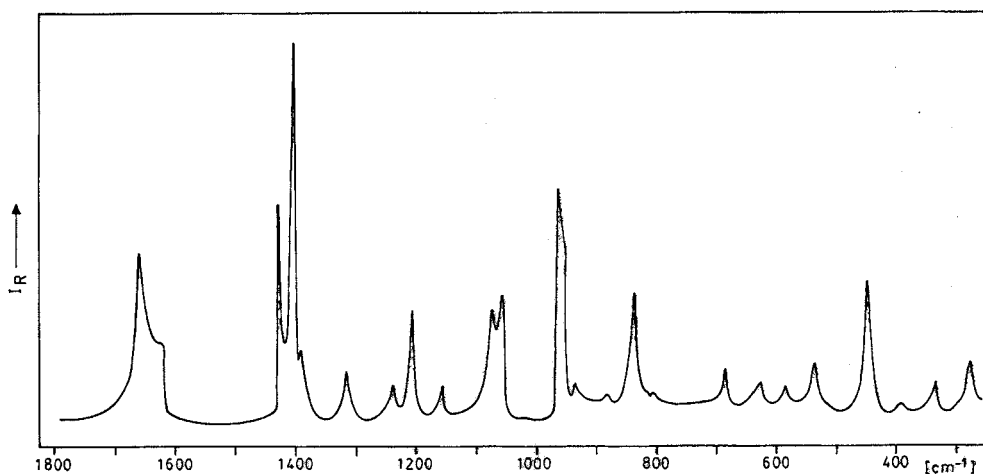


Fig. 2. Raman spectrum of  $K_2[Ni(C_6H_5O_7)(H_2O)_2]_2 \cdot 4H_2O$  in the range between 1800 and 250  $cm^{-1}$ .

Raman spectra) and a very strong and broad band centered at 3180  $cm^{-1}$  in the IR spectrum.

- Vibrations related to the  $\nu(CH_2)$  modes can only be seen as very strong Raman lines at 2946, 2937, and 2915  $cm^{-1}$  and are surely overlapped in the IR spectrum by the broad water absorption, which extends up to 2900  $cm^{-1}$ .

Table 1  
Assignment of the IR and Raman Spectra  
of  $K_2[Ni(cit)(H_2O)_2]_2 \cdot 4H_2O$  (Band Positions in  $cm^{-1}$ )

Infrared	Raman	Assignment
3511 s	3508 m	$\nu(OH)_{alcohol}$
3447 m, 3180 vs,br	3445 m	$\nu(OH)_{water}$
	2946 vs, 2937 s, 2915 vs	$\nu(CH_2)$
1650sh, 1612vs, 1559vs	1655 s, 1622 sh	$\nu_{as}(COO^-)$
1422 sh, 1409 vs	1428 s, 1407 vs	$\nu_s(COO^-)$
1382 s, 1357 sh	1390 w	+ $\delta(CH_2)_{sciss.}$
1422 sh	1319 w	
1276 vs	-----	$\delta(C-OH)_{alcohol}$
-----	1238 vw, 1213 m	
1153 m	1152 w	$\nu_{out\ of\ phase}(CCO)_{alcohol}$
1113 m	-----	
1068 s	1074 s, 1060 s	$\nu(C-C)$
981 sh, 964 m, 932 w	965 s, 935 vw	
-----	878 vw	
921 m	-----	
884 s	-----	$\nu(C-C)$
835 m, 823 w	841 s, 805 sh	$\nu_{in\ phase}(CCO)_{alcohol}$
779 m	-----	$\rho(CH_2)$
736 m, 728 m	-----	$\rho(H_2O)$
680 m, 667 w	683 w	$\delta(COO^-)$
634 s, 618 sh	628 w	$\delta(COO^-)$
-----	588 vw	
544 m,br, 525 sh, 469 m	538 w, 450 s	$\nu(Ni-O)$
398 w, 381 w	382 vw	
352 s, 333 w	330 w	$\rho(H_2O)$

Note: vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

- The antisymmetric stretching vibrations of the carboxylate groups are seen as a very strong and broad doublet (with a shoulder on the higher-intensity side) in the IR spectrum and as a doublet in the Raman spectrum. The IR components are surely additionally broadened because of the presence of the bending motion of the  $H_2O$  molecules, which lie in this same range.

- The corresponding symmetric stretching of these acidic groups generates the most intense Raman line ( $1407\text{ cm}^{-1}$ ) and a band multiplet in the IR spectrum, which is surely complicated by the superposition with one of the  $\text{CH}_2$  deformational motions.
- A further analysis of these carboxylate stretching vibrations shows that they appear in the range characteristic for unidentate bonded carboxylic groups. Using the two most intense and well-defined Raman lines for such an analysis, it can be shown that the difference between both stretchings ( $248\text{ cm}^{-1}$ ) is also typical for unidentate bonding (15).
- One deformational mode as well as two skeletal CCO modes, involving the alcoholic function, could be identified. Not all of the remaining bands in the medium spectral range could be unambiguously assigned; however, a pair of bands related to  $\nu(\text{C—C})$  stretchings and one rocking mode of the  $\text{CH}_2$  groups could be identified. The strong Raman band located at  $965\text{ cm}^{-1}$  can also be related to a  $\nu(\text{C—C})$  mode. In the range below  $700\text{ cm}^{-1}$ , we have assigned two  $\delta(\text{COO}^-)$  deformational modes.
- In relation to the metal-to-ligand vibrations, we could identify four rocking modes of the water molecules. Those lying at higher wave numbers may be related to the molecules bonded directly to the Ni(II) cations, whereas the other two are probably related to crystal water (16). On the other hand,  $\nu(\text{Ni—O})$  vibrations were assigned in the region between  $544$  and  $450\text{ cm}^{-1}$ . The IR band at  $544\text{ cm}^{-1}$  with a shoulder at  $525\text{ cm}^{-1}$  as well as the weak Raman band at  $538\text{ cm}^{-1}$  are probably related to carboxylate oxygen atoms. The remaining bands may be related to bonds involving water O atoms.

### **Magnetic Behavior**

As the structural analysis has shown a dimeric structure, it was interesting to investigate the existence of any type of magnetic interaction between both metallic centers.

An analysis of the temperature dependence of the molar magnetic susceptibility shows that the susceptibility obeys the Curie–Weiss law in the fully investigated temperature range between 1.9 and 300 K. In Fig. 3, we present a plot of the reciprocal magnetic susceptibility as a function of the temperature. From this plot, we deduced that  $\chi^{-1} = 0.9713 + 0.3933T$  and the effective magnetic moment for each of the Ni(II) ions has a value of 3.18 BM, which agrees very well with the experimental values usually found for isolated  $d^8$  species, without any type of magnetic interactions (17,18). On the other hand, the Weiss temperature,  $\theta$ , of only  $-1.03\text{ K}$ , additionally confirms the absence of magnetic interactions (18,19).

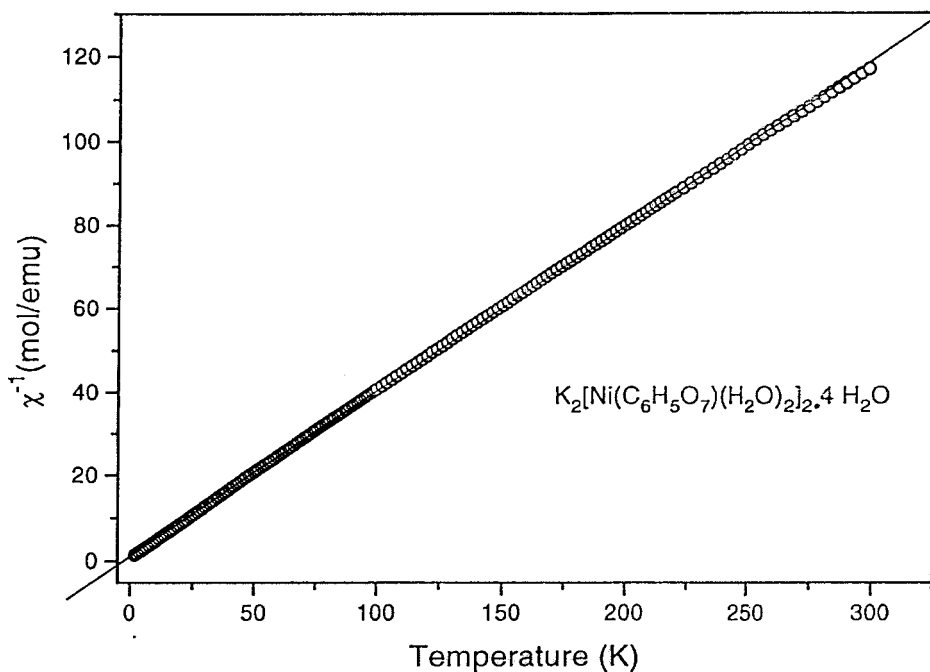


Fig. 3. Variation of the reciprocal magnetic susceptibility against temperature for  $K_2[Ni(C_6H_5O_7)(H_2O)_2]_2 \cdot 4H_2O$ .

## CONCLUSIONS

The most important and characteristic bands of the vibrational (infrared and Raman) spectra of  $K_2[Ni(C_6H_5O_7)(H_2O)_2]_2 \cdot 4H_2O$  could be assigned on the basis of the structural peculiarities of the complex. Information on the metal-to-ligand interactions could also be obtained from these spectra. Magnetic susceptibilities, measured between 1.9 and 300 K, show conclusively the absence of magnetic interactions, despite the presence of two bonded Ni(II) centers in the structure.

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