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Vibrational Behavior of Transition Metal Cupferronato Complexes: Raman Studies on Cobalt(II) Cupferronato Derivatives

M. Bolboaca^a; S. Cinta^a; M. Venter^b; A. Deak^b; I. Haiduc^b; O. Cozar^a; T. Iliescu^a; P. Rösch^c; W. Kiefer^c

^a Physics Department, Babes - Bolyai University, Cluj, Napoca, Romania ^b Chemistry Department, Babes - Bolyai University, Cluj, Napoca, Romania ^c Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, Würzburg, Germany

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**VIBRATIONAL BEHAVIOR OF TRANSITION METAL
CUPFERRONATO COMPLEXES: RAMAN STUDIES ON COBALT(II)
CUPFERRONATO DERIVATIVES**

Key Words: Raman spectroscopy, cupferron, Co(II) cupferronato complexes.

**M. Bolboaca^a, S. Cinta^a, M. Venter^b, A. Deak^b, I. Haiduc^b, O. Cozar^a,
T. Iliescu^a, P. Rösch^c, and W. Kiefer^{c*}**

^a*Babes – Bolyai University, Physics Department, 3400 Cluj – Napoca, Romania*

^b*Babes – Bolyai University, Chemistry Department, 3400 Cluj–Napoca, Romania*

^c*Institut für Physikalische Chemie, Universität Würzburg, Am Hubland, D-97074
Würzburg, Germany*

ABSTRACT

The FT-Raman spectrum of cupferron, $[\text{PhN}_2\text{O}_2]\text{NH}_4$ and the micro-Raman spectra of the new corresponding cobalt(II) cupferronato complexes, CoL_2A_2 , $\text{L} = \text{PhN}_2\text{O}_2^-$, $\text{A} = \text{H}_2\text{O}$, MeOH , $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ and CoL_2A , $\text{A} = (-\text{C}_6\text{H}_4\text{NH}_2\text{-}p)_2$ were recorded and discussed. All the complexes show a Raman band at about 1302 cm^{-1} and the characteristic $\nu(\text{N-N})$ and $\delta(\text{ONNO})$ modes of the anionic ligand. The vibrational analysis of the title compounds reveals the electron delocalisation over the N-nitroso-N-hydroxylaminato (ONNO) unit, as well as the bidentate coordination of the cupferronato ligand to the metal center through the oxygen atoms.

INTRODUCTION

The salt of N-nitroso-N-phenylhydroxylamine [PhN_2O_2] NH_4 (cupferron) is a well known analytical reagent (FIG. 1, a). Additionally, the cupferron is a biologically active compound, known to display carcinogenic, genotoxic, mutagenic and DNA-damaging effects¹. The N-nitroso-N-phenylhydroxylaminato (cupferronato) anion (PhN_2O_2^-) has been extensively used as ligand in coordination chemistry, acting mostly as bidentate chelating or bridging ligand¹.

We become interested in cobalt (II) cupferronato complexes with different neutral donor molecules (e.g. water, methanol, *o*-diaminobenzen, *p*-diaminobenzen, benzidine) since only one related compound, $\text{Co}(\text{PhN}_2\text{O}_2)_2(\text{MeOH})_2$ was structurally investigated so far² (FIG. 1, b). The cupferron and the corresponding main group metal complexes were investigated by Raman spectroscopy, and the selected vibrational data were reported^{1,3,4}. A detailed Raman analysis could provide important and rich information about the coordination pattern and the structure of the cupferronato ligand bind to cobalt.

Here we report the first Raman studies on N-nitroso-N-phenylhydroxylaminato (cupferronato) cobalt(II) complexes: diaqua-bis-cupferronato-cobalt(II), $\text{CoL}_2(\text{H}_2\text{O})_2$ (**1**), dimethanol-bis-cupferronato-cobalt(II), $\text{CoL}_2(\text{MeOH})_2$ (**2**), di-*o*-diaminobenzene-bis-cupferronato-cobalt(II), $\text{CoL}_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{NH}_2)_2$ (**3**), di-*p*-diaminobenzene-bis-cupferronato-cobalt(II), $\text{CoL}_2(p\text{-NH}_2\text{C}_6\text{H}_4\text{NH}_2)_2$ (**4**) and benzidine-bis-cupferronato-cobalt(II), $\text{CoL}_2(p,p'\text{-NH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2)_2$ (**5**), where $\text{L} = \text{PhN}_2\text{O}_2^-$. Further structural investigations based on physical and spectral (IR, ESR and X-ray diffraction analysis) data are in progress.

EXPERIMENTAL

The starting materials were obtained from commercial sources (Aldrich) as analytical pure reagents. The complex **1** was prepared by the reaction of cupferron with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in water, at room temperature. The reaction of **1** with different

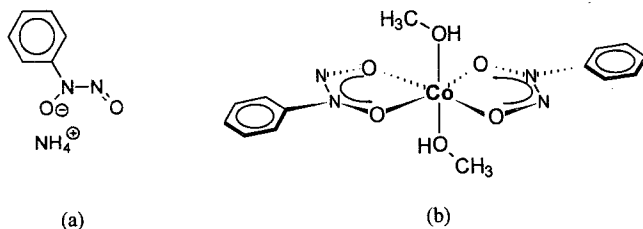


FIG. 1. Schematic drawing of cupferron ($\text{NH}_4\text{PhN}_2\text{O}_2$) (a) and the corresponding $\text{Co}(\text{PhN}_2\text{O}_2)\text{MeOH}_2$ complex (b).

neutral donors (methanol, *o*-diaminobenzene, *p*-diaminobenzene and benzidine) in ethanol, at room temperature, yielded the complexes **2-5** in microcrystalline state. The spectral purity of **1-5** is supported by elemental analysis.

For recording the absorption spectra we prepared 10^{-3} mol l^{-1} ethanol solution for each complex. The absorption spectra of cupferron and complexes **1-5** were recorded with a Perkin Elmer Lambda 19 UV-VIS-NIR spectrometer with a scan speed of 240 nm/min.

The FT-Raman spectrum of cupferron has been recorded using a Bruker IFS 120 HR spectrometer with an integrated FRA 106 Raman module. Radiation of 1064 nm from a Nd-YAG laser was employed for excitation with an output of 95 mW. A Ge detector operating at liquid nitrogen temperature was used. The spectral resolution was 3 cm^{-1} .

Only poor FT-Raman spectra of **1-5** were obtained. Therefore a higher energy excitation line was required. A Kr ion laser Spectra-Physics model 2020 was used for excitation of the micro-Raman spectra of complexes using the 647.09 nm line with an output power of 300 mW. The laser beam was carried through a filter prism (Anaspec) in order to avoid the plasma lines and then was focused with an Olympus ULWD MSPLAN 80 microscope objective on the powder sample. The back scattered light was collected by the same objective and after reflection by a beam-splitter, focused with a lens ($f=150\text{ mm}$) on the entrance slit of a Spex

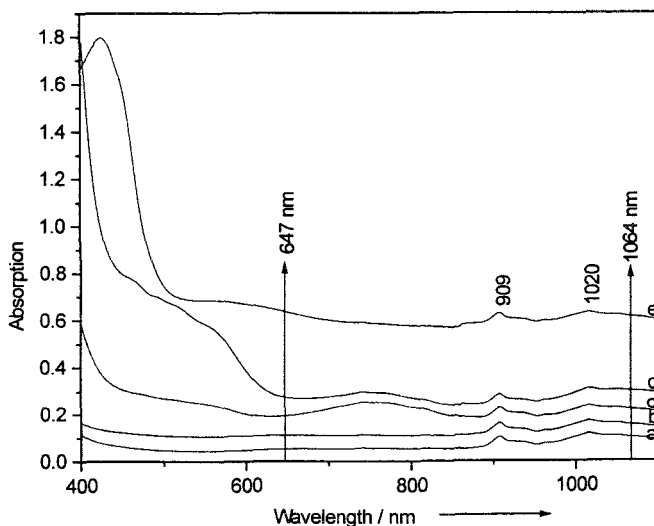


FIG. 2. Absorption spectra of $\text{CoL}_2(\text{H}_2\text{O})_2$ (a), $\text{CoL}_2(\text{MeOH})_2$ (b), $\text{NiL}_2(o\text{-NH}_2\text{-Py})_2$ (c), $\text{NiL}_2(\text{H}_2\text{O})_2$ (d), $\text{NiL}_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{NH}_2)_2$ (e), $\text{L} = \text{PhN}_2\text{O}_2^{-1}$, $\text{Py} = \text{pyridine}$, $10^{-3} \text{ mol l}^{-1}$ ethanol solution.

Model 1404 double monochromator equipped with 1800 grooves/mm holographic gratings. A Photometrics Model 9000 CCD camera detection system and analyzing software package (MAPS V1.0) were employed for acquisition of data. The spectra were taken with a resolution of 2 cm^{-1} for this case.

RESULTS AND DISCUSSION

The absorption spectra of the complexes **1-5** were very similar. Figure 2 presents the absorption spectra of five cupferronato complexes. The electronic absorption peaks of the samples under study are located at 909 and 1020 nm, respectively. Therefore, we assume that a resonance or preresonance contribution to the Raman intensity is not significant, nor was it demonstrated in further investigation using the green laser line⁵.

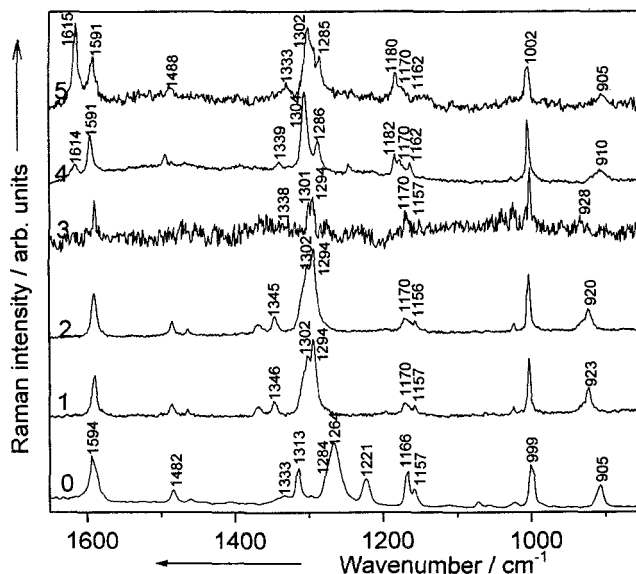


FIG.3. FT-Raman spectrum of $\text{Ph}[\text{N}_2\text{O}_2]\text{NH}_4$ (0) and micro-Raman spectra of $\text{CoL}_2(\text{H}_2\text{O})_2$, (1) $\text{CoL}_2(\text{MeOH})_2$, (2) $\text{CoL}_2(o\text{-NH}_2\text{C}_6\text{H}_4\text{NH}_2)_2$, (3) $\text{CoL}_2(p\text{-NH}_2\text{C}_6\text{H}_4\text{NH}_2)_2 \cdot 1/2\text{CHCl}_3$, (4) $\text{CoL}_2(p,p'\text{-NH}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NH}_2)_2$, (5); $\text{L} = \text{PhN}_2\text{O}_2^-$. Laser line 1064 nm, $P = 96.4$ mW, (0), 647 nm, $P = 300$ mW (1-5).

The Raman spectra of cupferron and the new cobalt(II) cupferronato complexes (1-5), recorded in the spectral range $1650\text{--}850\text{ cm}^{-1}$, are presented in FIG. 3. In the spectral region $1650\text{--}3600\text{ cm}^{-1}$, for the complexes 3-5 bands appear due to the amino-donor molecules⁶, which are not shown here and for the other two complexes this region is not significant. The observed bands in the region of $850\text{--}1650\text{ cm}^{-1}$ with the tentative assignment are summarized in Table 1.

The following discussion is based on the comparison of the spectra of complexes 1-5 to that of cupferron. Many similarities, as well as some specific differences can be observed. The assignment of the $\nu(\text{N-N})$ and $\delta(\text{N}_2\text{O}_2)$ vibrational modes, specific for the cupferron at 1333 and 905 cm^{-1} , respectively,

TABLE 1

Vibrational Raman and IR Data (cm^{-1}) of Cupferron (NH_4L , $\text{L} = \text{PhN}_2\text{O}_2^-$) and corresponding Co(II) complexes: CoL_2A_2 , $\text{A} = \text{H}_2\text{O}$ (1), MeOH (2), *o*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ (3), *p*- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ (4) and CoL_2A , $\text{A} = (-\text{C}_6\text{H}_4\text{NH}_2-p)_2$ (5).

IR [1]	Raman	Raman					Vibrational Assignment
NH_4L		1	2	3	4	5	
					1614w ^a	1615vs	$\delta(\text{NH}_2)$
1595w	1594s	1592s	1592s	1591s	1591m	1591m	quadrant ring stretch
1490m	1482w	1484w	1484w	1486w	1488w	1488w	semicircle ring stretch
1335s	1333w	1346m	1345m	1338w	1339m	1333m	$\nu(\text{N-N})$
1310s	1313s						$\nu(\text{ONNO})$
		1302s	1302s	1301s	1304vs	1302vs	$\nu_{\text{sym}}(\text{ONNO})$
	1284sh	1294vs	1294vs	1294s	1286s	1285s	$\nu(\text{C-N})$
1270vs	1264vs						$\nu(\text{N=O})$
1220vs	1221m						
1170w	1166s	1170m	1170m	1170m	1182m	1180m	$\delta(\text{C-H})$ of C_6H_5 and C_6H_4
1160w	1157m	1157w	1156w	1157w	1162m	1162w	$\delta(\text{C-H})$
	999s	1001s	1001s	1001vs	1002s	1002s	ring breathing
910	905m	923m	920m	928m	910m	905m	$\delta(\text{ONNO})$

^aAbbreviations:

vs- very strong, s-strong, m-medium, w-weak, sh-shoulder, ν -stretching, δ -bending.

is in good agreement with the corresponding IR data^{1,4,7,8}. In addition, the $\nu(\text{N}=\text{O})$ mode provides two bands at 1264 and 1221 cm^{-1} , respectively, due to the *cis-trans* configuration of the N-nitroso-N-hydroxylaminato group (ONNO) in cupferron⁹. After coordination, the *cis*-configuration of the ligand is expected to be present in the title complexes². Comparing the Raman spectra of **1-5** to that of the ligand, significant changes in the position and relative intensities of the mentioned bands can be observed. Thus, the $\nu(\text{N}-\text{N})$ and $\delta(\text{ONNO})$ modes are shifted to higher wavenumbers up to 1346 and 928 cm^{-1} , respectively.

Analogue to the tin(IV) and nickel(II) cupferronato complexes, where the $\nu(\text{N}=\text{O})$ modes are located at around 1215 cm^{-1} as weak or very weak bands^{1,10}, similar corresponding signal is observed in the Raman spectra of the Co(II) cupferronato complexes. A strong band and a shoulder are located in the spectrum of cupferron at 1313 and 1284 cm^{-1} . The first one is observed in the spectra of all complexes, shifted to lower wavenumbers by 9-12 cm^{-1} . This band, considered as a fingerprint, was also noticed in a previous Raman report on main group metal cupferronates³, being tentatively assigned to the new symmetric mode of the coordinated ONNO unit. The shoulder was assigned in the spectrum of the ligand to the $\nu(\text{C}-\text{N})$ mode^{9,10}. In the spectra of complexes **1-5** appears a band that is constantly shifted to higher wavenumbers by 1-10 cm^{-1} due to the involvement of the C-N bond in the electron delocalisation.

The characteristic vibrational modes of aromatic groups were observed in the expected spectral regions^{6,10} (FIG. 3), the most representative being assigned to the ring stretching (1594-1591, 1488-1482 cm^{-1}) and ring breathing (1002-996 cm^{-1}) modes. Supplementary, the neutral donor molecules coordinated to the metal center bring new contributions^{6,10} at about 1615 and 1180 cm^{-1} in the spectra of **4** and **5**.

CONCLUSIONS

In conclusion, FT- Raman spectra of the cupferron exhibit the typical $\nu(\text{N}-\text{N})$,

$\nu(\text{N}=\text{O})$ and $\delta(\text{ONNO})$ modes. The vibrational behavior of the cupferronato anion bound to the metal center confirms the electron delocalisation over the ONNO unit, as well as the bidentate coordination pattern. Furthermore, the band at about 1302 cm^{-1} , assigned to a new symmetric vibrational mode of the ligand, is representative for all the cupferronato cobalt(II) complexes. In order to extend the vibrational studies on metal cupferronato complexes and to bring new information about their molecular structure, further Raman and SERS investigations on nickel(II) homologues are in progress⁵.

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