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Infrared and Raman spectra of $[Re(CN)_5NO]^{3-}$ complex isolated in KCl matrix

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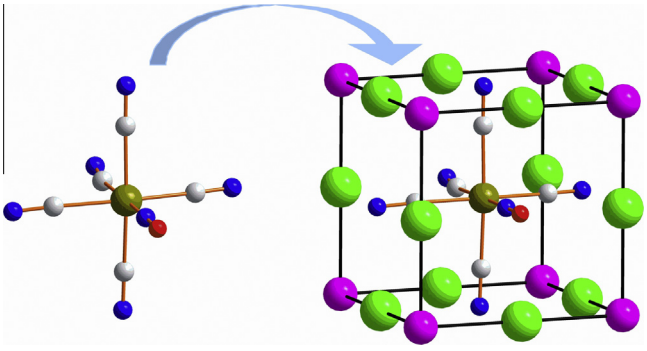
HIGHLIGHTS

- Inclusion of $[Re(CN)_5NO]^{3-}$ ion in KCl matrix is evidenced by XRD, IR and Raman.
- The Raman spectrum of the complex in solid state is reported for the first time.
- Complex diluted in KCl affords an improved assignment of $[Re(CN)_5NO]^{3-}$ modes.
- Diamagnetic behavior of $[Re(CN)_5NO]^{3-}$ confirms Re(I): $[Xe]4f^{14}5d^6$ ground state.

GRAPHICAL ABSTRACT

Schematic included $[Re(CN)_5NO]^{3-}$ complex in a KCl matrix.



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ABSTRACT

We report here the infrared and Raman spectra of $[Re(CN)_5NO]^{3-}$ complex as guest diluted in the KCl crystal lattice. According to the chemical analysis, the anion concentration in the KCl host matrix is in excess of 2% (in mole). The solid state Raman spectrum of this complex is reported for the first time. The information obtained from the relative intensities of infrared and Raman bands affords a reexamination of vibration mode assignments. The observed bands splitting may be explained by the interactions of the guest complex with the host lattice, including the ways in which the K^+ vacancies are distributed around $[Re(CN)_5NO]^{3-}$ to achieve lattice charge neutrality.

Introduction

Interest in transition metal nitrosyls has increased in the last years due to the important role that nitric oxide (NO) plays in biological systems. NO can be generated by hydrolysis of some transitions metal complexes containing nitrosyl ligand [1].

Transition metal nitrosyls have additional interest because some of them show two metastable states (photoisomers) when irradiated at low temperatures with light in the visible or ultraviolet region. Most of the transition metals that showed this property belong to group 8 (Fe, Ru, Os) [2]. Two metastable states were also reported for NiCpNO (Cp: cyclopentadienyl) [3] and one in $K_3[Mn(CN)_5NO].2H_2O$ [4] and $K[IrCl_5NO]$ [5].

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In our quest for further systems that could exhibit metastability we are exploring here the scarcely studied rhenium(I) nitrosyl complex, $[Re(CN)_5NO]^{3-}$, in its ground state. The synthesis of salts of this complex in the form of single crystals adequate for a complete structure determination and spectroscopic characterization proved elusive. Instead we obtained solid solutions of $[Re(CN)_5NO]^{3-}$ ion diluted in a KCl matrix.

We report here X-ray diffraction, spectroscopic and magnetic evidence of the octahedral $[Re(CN)_5NO]^{3-}$ complex included as a dilute guest anion in cubic KCl host crystal, an unusual system in which the structure and charge of the guest and host are dissimilar. We also report the infrared (IR) and Raman spectra and the vibrational mode assignment for the included rhenium(I) complex.

Experimental

Preparation

When attempting the synthesis of the target $K_3[Re(CN)_5NO]$ solid, using the method reported in [6], single crystals were obtained after double re-crystallizing by slow evaporation from aqueous solutions of the reaction products. Selected orange cubic-shaped crystals were then separated from the solution for structural X-ray diffraction, infrared and Raman spectroscopy, and magnetic studies.

X-ray diffraction data

The measurements were performed on an Oxford Xcalibur Gemini, Eos CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. X-ray diffraction intensities were collected (ω scans with ϑ and κ-offsets), integrated. and scaled with CrysAlisPro suite of programs [7]. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlisPro. Data were corrected empirically for absorption employing the multi-scan method also implemented in CrysAlisPro. The structure was refined by full-matrix least-squares procedure on F^2 with SHELXL-97 [8]. Crystal data and refinement results are summarized in Table 1.

Table 1
Crystal data and structure refinement results for the KCl host.

Empirical formula	KCl
Formula weight	74.55
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system, space group	Cubic, Fm-3 m (#225)
Unit cell dimensions	$a = 6.3158(8)$ Å
Volume	251.93(6) Å^3
Z, Calculated density	4, 1.965 Mg/m^3
Absorption coefficient	2.744 mm^{-1}
F(000)	144
Crystal size	0.10 × 0.10 × 0.10 mm
Crystal color	Orange
θ-range for data collection	5.59–27.64°
Limiting indices	$-6 \leqslant h \leqslant 8$, $-7 \leqslant k \leqslant 8$, $-7 \leqslant l \leqslant 8$
Reflections collected/unique	289/28 [R(int) = 0.0085]
Completeness to $\theta = 27.64°$	96.6%
Max. and min. transmission	0.7729 and 0.7729
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	28/0/3
Goodness-of-fit on F^2	1.321
Final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0094$, $wR_2 = 0.0229$
R indices (all data)	$R_1 = 0.0094$, $wR_2 = 0.0229$
Largest diff. peak and hole	0.068 and −0.103 e.Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2]^{1/2}$.

Chemical analysis

Chloride contents were determined by isocratic ionic chromatography (anionic DIONEX AS4A column). 0,413 mg of chloride were found per mg of sample. The complex content in the solid solutions were measured through the Carbon and Nitrogen determination using a Carlo Erba (Milan, Italy) EA 1108 elemental analyzer. The samples from different re-crystallizations showed varying degrees of complex concentrations. For the more diluted one, we obtained Anal. Exp.: C, 1.3; N, 1.6% values that lead to a mole ratio of 1:50 (2% in mole) for $[Re(CN)_5NO]^{3-}$ in KCl matrix.

IR and Raman spectroscopy

The infrared spectra (KBr pellets, 4000–200 cm^{-1}) were recorded with a FTIR Bruker 113v spectrometer equipped with a mid IR DTGS detector. Raman spectra of powdered sample were obtained at room temperature with a FTIR Bruker 66 spectrometer fitted with the NIRR attachment. Infrared and Raman spectra were collected at 4 cm^{-1} resolution.

Magnetic measurements

Room temperature magnetic measurements were carried out using a commercial vibrating sample magnetometer (LakeShore 7404) with up to 19 kGs magnetic field strength.

Results and discussion

Fig. 1 shows typical single crystals obtained as product of our reaction. Single crystal X-ray diffraction pattern revealed instead a cubic potassium chloride structure with cell dimension $a = 6.3158(8)$ Å, very close to that for pure KCl [6.2917(3) Å] [9]. Table 2 shows the corresponding atomic fractional coordinates and isotropic displacement parameters.

The residual electron density observed in the final difference Fourier map is less than 0.07 e.Å^{-3}. This, in conjunction with the vibrational data, magnetic measurements (see below), and the color exhibited by the crystals, demonstrated that the $[Re(CN)_5NO]^{3-}$ complex enters the host KCl lattice as an impurity. Probably, $[Re(CN)_5NO]^{3-}$ ion acts as a guest in the KCl lattice at an octahedral site replacing a $[KCl_6]^{5-}$ group as may be concluded comparing the estimated maximum transversal N–C–Re–C–N dimension (~9.358 Å), obtained for $[Re(CN)_5NO]^{2-}$ [10] (considering a van der Waals radii of 1.4 Å for the terminal nitrogen atoms) with

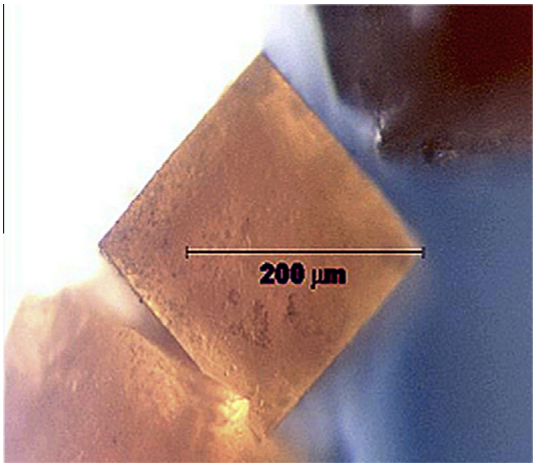

Fig. 1. Photos of selected crystals of $[Re(CN)_5NO]^{3-}$ complex in KCl matrix.

Table 2
Atomic coordinates and isotropic displacement parameters ($Å^2 \times 10^3$) for KCl host.

Atom	x	y	z	U
Cl	0	0	0	24(1)
K	1/2	1/2	1/2	24(1)

the Cl···Cl distance of 9.936 Å (van der Waals radii of 1.8 Å for Cl^- ion) in the KCl host matrix. Therefore, the complex comfortable fit into the hole left by the replaced $[KCl_6]^{5-}$ octahedron. The lattice local charge neutrality could be restored by a pair of K^+ vacancies in the $[Re(CN)_5NO]^{3-}$ neighborhood. This can be understood as due to the local C_{4v} symmetry imposed by the impurity yielding complex–matrix interactions that may include subtle further distortions of the anion at the lattice site. In turn, this would explain some splitting found in vibrational bands assigned to ν(NO), ν(CN) and other modes observed in the IR and Raman spectra (see below). Previously, our group succeeded in incorporating another pentacyanonitrosyl metallate, namely nitroprusside ($[Fe(CN)_5NO]^{2-}$) ion, as a guest in orthorhombic hexacyanometallate(III) (metal: Fe, Co) host matrices with concentrations of up to 12%, but in this case the nature of the guest and host are very similar [11].

Infrared and Raman spectra

Fig. 2 shows the infrared and Raman spectra of $[Re(CN)_5NO]$-containing orange crystals. Assignments of observed bands are collected in Table 3.

CN stretching bands in transition metal complexes can be identified because they exhibit sharp features in the 2200–2000 cm^{-1} spectral region, either for infrared and Raman spectra [14]. However, in our compound the bands assigned to ν(CN) measured at relatively lower frequencies can be explained due to back-bonding of the CN group as consequence of the low oxidation state of Re.

The weak infrared band observed at 2032 cm^{-1} is assigned to ν(^{13}CN) mode. This is sustained by a simple calculation based on a diatomic model and referred to the strong ν(^{12}CN) band at 2078 cm^{-1} which leads to an isotopic red-shifted frequency of 2034 cm^{-1}, in good agreement with the observed value. Further evidence of the assignment is provided by the observed integrated intensity band ratio of 1.1%, a percentage close to ^{13}C natural abundance.

In transitions metal nitrosyl complexes, N–O stretching bands are found in the 2000–1500 cm^{-1} region. These modes are easily recognizable because they are intense and broad in the infrared absorption spectra and very weak in Raman spectra [14–16]. This behavior, which was also observed by us in the studied compound, gives further evidence of the molecular insertion of $[Re(CN)_5NO]^{3-}$ ion in the KCl lattice.

NO stretching modes are more sensitive to back-bonding effect than in CN stretch, particularly when the transition metal ion is in a low oxidation state as in our case for Re(I). Therefore, the relatively low frequency observed for this mode (~1650 cm^{-1}) is again attributed to a back-bonding effect.

ν(MN) stretching and δ(MNO) deformation bands are observed in the 700–600 cm^{-1} region. Both modes show up as sharp and medium-intensity bands both in infrared and Raman spectra. For a series of transition metal nitrosyls [15–19] δ(MNO) modes show relatively strong absorption bands in infrared and weak scattering features in Raman. The opposite behavior is observed for ν(MN) modes. They show up as relatively strong bands in Raman and as weak absorptions in infrared. Assuming the same behavior for the $[Re(CN)_5NO]^{3-}$ anion we assigned the bands at 627 and 604 cm^{-1} to δ(ReNO) and ν(ReN) modes, respectively.

We hypothesize that these assignments differ from those reported by Bhattacharyya and Roy [6] because Raman spectra were not available to the authors. These modes were not clearly assigned neither in [12] nor [13] (see Table 3). ν(MC), δ(MCN), δ(CMC), δ(CMN) and combination modes appear in the region below 550 cm^{-1}.

Revised assignments given in Table 3 are compared with those reported in the literature for the potassium salt of $[Re(CN)_5NO]^{3-}$. Bands positions are similar to those reported before in [6,12,13] but differ in the fine structure because in our crystallized system the $[Re(CN)_5NO]^{3-}$ anion locally undergoes subtle perturbations not found in the pure compound. Splitting of ν(CN), ν(NO) and other modes may be explained by different host crystal field effects acting on the complexes.

Raman positions were reported previously for the anion in aqueous solution [12]. In this work sample decomposition was observed for exciting beam light of 647.1 or 568.2 nm wavelengths. Raman measurements, reported here for the first time in the solid state, were feasible in our samples due to dilution of the complex in the crystal matrix, as well as to the use of a different exciting laser light (λ = 1064 nm) that avoided chemical decomposition.

Magnetic results

To confirm the low spin Re(I): $[Xe]4f^{14}5d^6$ ({ReNO}^{6} [20]) ground state electronic configuration in the [Re(CN)5NO]$^{3-}$ complex, magnetic measurements were performed to compare the pure diamagnetic KCl crystal with KCl samples hosting the com-

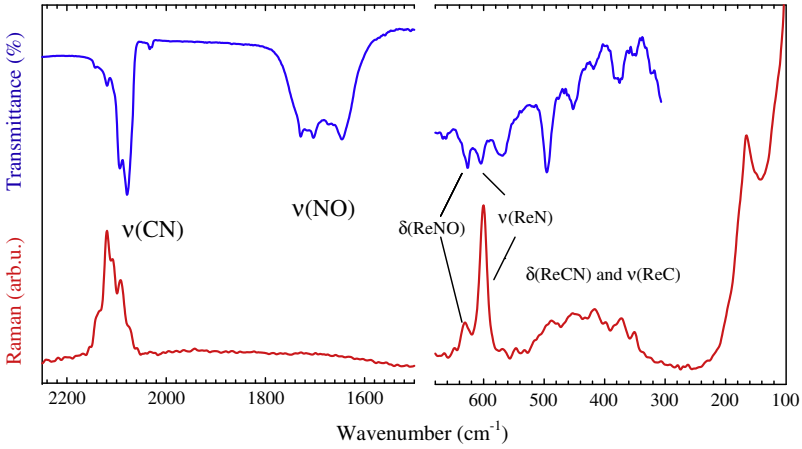

Fig. 2. Infrared and Raman spectra of $[Re(CN)_5NO]^{3-}$ guest isolated in KCl host crystal.

Table 3
Frequency (in wavenumbers, cm^{-1}) and assignment of vibration modes for the infrared and Raman spectra of $[Re(CN)_5NO]^{3-}$ in KCl matrix and comparison with previous studies reported in the literature.

Present compound		Compound of Griffith[12]		Bhattacharyya et. [6]	Sergeeva et. al.) [13]	Assignment
Infrared	Raman	Infrared	Raman	Infrared	Infrared	
2140(vw), 2119(w), 2092(s), 2078(s)	2137(sh), 2120(s), 2109(w), 2092(m) 2073(sh)	2141(m), 2110(m), 2080(s), 2045(s)	2135(m) 2115(s), 2090(m)	2170(m), 2120(w), 2075(s), 2050(sh)	2090, 2110	ν(CN)
2032						ν(^{13}CN)
1727(s), 1702(s), 1677(w), 1645(s), 1575(w)	----	1650(s)	1640	1650(s)	1730	ν(NO)
627(w)	631(w)	632	621(m)	495(w)		δ(ReNO)
604(vw)	600(m)	594	602(s)	620(sh)		ν(ReN)
526(w)					518	ν(ReC) and δ(ReCN)
495(m)	487(w)	480(s)				
450(w)	452(w)	445(s)	442(w)	450(w)	445	
419(w)	417(vw)	425(m) 398(m)	412		405	
379(w)	372(w)	375(m)	370			
350(w)	351(vw)	362(m) 310		360(w)		
	166(m)					Lattice mode

s: strong, w: weak, sh: shoulder, v: very, m: medium.

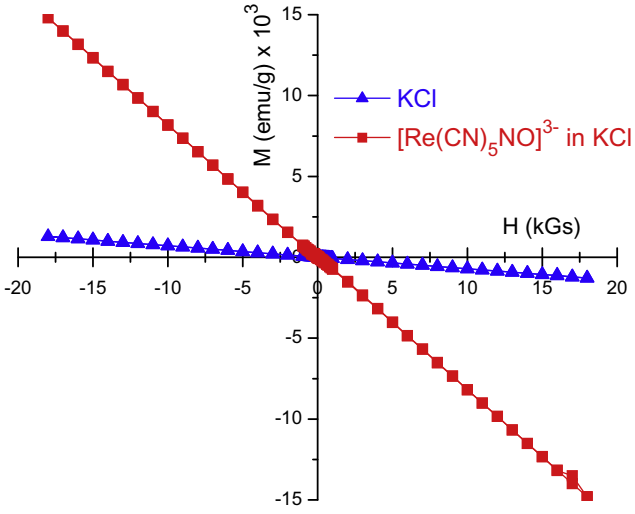

Fig. 3. Normalized magnetic moment (**M**) versus magnetic field (**H**) of pure KCl and $[Re(CN)_5NO]^{3-}$ containing KCl sample in the highest relative concentration.

plex as impurities in different concentrations, discriminated by their color intensity. We observed in the magnetic moment (M) versus magnetic field (H) plot that the negative slope increased with color intensity. This is expected for relative larger diamagnetic contribution of the complex in part due to its extended electronic MO. The results for the most strongly colored sample are compared in Fig. 3 with pure KCl. The qualitative magnetic measurements rule out the Re(II) paramagnetic electronic configuration [Xe]$4f^{14}5d^5$ ($Re(NO)^{3+}$), $\{ReNO\}^5$ [20] for all samples (cf [10]).

Conclusion

We present here X-ray diffraction, spectroscopic, chemical analysis and magnetic evidences on the inclusion of $[Re(CN)_5NO]^{3-}$ complex as a diluted guest in a KCl host matrix. Although the nature of the complex and KCl solid are very different, the co-crystallization is possible because size and charge compatibility of guest and host. Therefore, the octahedral $[KCl_6]^{5-}$ group of the KCl host could be replaced by the guest $[Re(CN)_5NO]^{3-}$ anion (Fig. 4). The

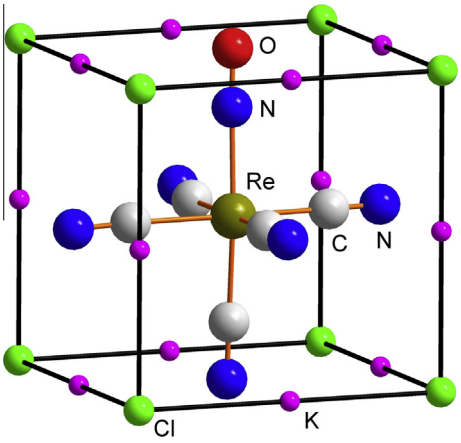

Fig. 4. Scheme showing a $[Re(CN)_5NO]^{3-}$ anion included in a KCl crystal lattice.

charge neutrality condition could be locally fulfilled by K^+ vacancies around the guest in the lattice.

The Raman spectra of the $[Re(CN)_5NO]^{3-}$ anion in a solid state environment is also reported. It affords a revised assignment of its vibration modes by comparing the infrared and Raman spectra of $[Re(CN)_5NO]^{3-}$ with the corresponding spectroscopic data of other similar and well-studied anions [15,16].

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