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Mössbauer Spectroscopic Studies of the Alkali Metal and Transition Metal Nitroprussides[1]

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Mössbauer spectra of several structurally related alkali metal nitroprussides, $M_2[Fe(CN)_5NO] \cdot xH_2O$ (where M = Li, Na, K, Rb, Cs, NH_4, Ag, Cu), and divalent transition metal nitroprussides, $M[Fe(CN)_5NO] \cdot xH_2O$ (where M = Mn, Fe, Co, Ni, Cu, Zn, Cd), have been studied at room temperature. Except for ferrous nitroprusside which has four lines, all the other compounds show two-line spectra with large quadrupole splittings (ΔE_Q). Results on $Fe[Mn(CN)_5NO] \cdot 2H_2O$ are also presented. The influences of the outer cations on various Mössbauer parameters are not very pronounced.

Introduction

The Mössbauer spectrum of sodium pentacyanonitrosyl ferrate(II) dihydrate $Na_2[Fe(CN)_5NO] \cdot 2H_2O$, more commonly known as sodium nitroprusside,[2-11] has been of considerable interest ever since it was proposed[12-16] as a standard for nuclear isomer shift (δ) measurements with ^{57}Fe Mössbauer spectroscopy. Since 1962, when the first Mössbauer spectrum of sodium nitroprusside[2,3] was reported, several workers[17,18] have confirmed the results obtained by Kerler and Neuwirth.[2a] Recently Grant, Housley, and Gonser[11] have reported the value of quadrupole splitting ($\Delta E_Q = 1.7048 \pm 0.0025$ mm/sec) on the basis of single-crystal measurements and have calculated the value of the electric field gradient (EFG) asymmetry parameter, η, to be 0.01 ± 0.01. Some workers[19,20] have also investigated the aqueous and nonaqueous solutions of sodium nitroprusside and its reduction products in frozen state. Extensive molecular orbital calculations have been carried out by Manoharan and Gray.[21,22]

A literature survey shows[17,18] that among various nitroprussides, Mössbauer studies have been done only for the sodium and zinc compounds.[8] In the case of alkali metal ferrocyanides[23,24] and ferricyanides[25-27] there has been observed a marked influence of the electronegativity (χ) of the cation on various Mössbauer parameters. We therefore undertook to study such an effect for nitroprusside complexes containing monovalent and divalent metal, *viz.*, $M^I_2[Fe(CN)_5NO] \cdot xH_2O$ where M = Li, Na, K, Rb, Cs, NH_4, Ag, or Cu and $M^{II}[Fe(CN)_5NO] \cdot xH_2O$ where M = Mn, Fe, Co, Ni, Cu, Zn, or Cd and $Fe[Mn(CN)_5NO] \cdot 2H_2O$. Our attempts to study nitroprussic acid $H_2[Fe(CN)_5NO]$ for a possible hydrogen bonding were not successful because of difficulties in preparing the compound in the solid phase.

Experimental Section

Materials.—Reagent grade (E. Merck, Germany) sodium nitroprusside was used. It was recrystallized in aqueous solution for spectral measurements. For most preparations the respective metal chlorides were used (AnalaR grade, BDH, or S. Merck, India). Cuprous chloride was freshly prepared from cupric chloride.[28] Ethyl alcohol, acetone, and chloroform were all purified and dried before use in the synthesis.

Preparation of Compounds.—Nitroprussides, in general, have been well described by Williams[29] and several others.[30] The following procedure was adopted for the synthesis of individual nitroprussides.

Silver Nitroprusside, $Ag_2[Fe(CN)_5NO]$.—This was obtained as a reddish pink precipitate when sodium nitroprusside (0.1 mol) and $AgNO_3$ (0.2 mol) dissolved in water were mixed. The silver nitroprusside so obtained was further used in synthesizing other monovalent nitroprussides as follows.

Alkali Metal Nitroprussides.—All the alkali metal nitroprussides were prepared by the double-decomposition reaction of the silver nitroprusside (0.01 mol) and the corresponding alkali metal chloride (0.02 mol) (eq 1) and filtering out the precipitated silver chloride. The filtrate was kept for slow evaporation at 50–55° under an infrared lamp and fine needle-shaped crystals were obtained.

$$Ag_2[Fe(CN)_5NO] + 2MCl \longrightarrow M_2[Fe(CN)_5NO] + 2AgCl \quad (1)$$
$$(M = Li, K, Rb, Cs, NH_4, Tl)$$

Transition Metal Nitroprussides.—All the transition metal nitroprussides were prepared by precipitation reaction using

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TABLE I

MÖSSBAUER PARAMETERS FOR VARIOUS NITROPRUSSIDES

Compd	Color	Isomer shift,[a] δ, mm/sec	Quadrupole splitting, ΔE_Q, mm/sec	Line widths (fwhm), Γ_1 and Γ_2, mm/sec
$Li_2[Fe(CN)_5NO]\cdot 3H_2O$	Brown-red	0.05 ± 0.02	1.62 ± 0.03	0.26, 0.24
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	Ruby red	0.00 ± 0.02	1.71 ± 0.02	0.24, 0.26
$K_2[Fe(CN)_5NO]\cdot 2H_2O$	Dark red	0.07 ± 0.02	1.74 ± 0.03	0.30, 0.32
$(NH_4)_2[Fe(CN)_5NO]\cdot H_2O$	Red	0.14 ± 0.02	1.50 ± 0.02	0.20, 0.22
$Rb_2[Fe(CN)_5NO]$	Red	0.13 ± 0.02	1.78 ± 0.02	0.26, 0.24
$Cs_2[Fe(CN)_5NO]$	Red	0.40 ± 0.02	2.00 ± 0.03	0.24, 0.22
$Ag_2[Fe(CN)_5NO]$	Reddish pink	0.10 ± 0.02	1.54 ± 0.03	0.26, 0.26
$Cu_2[Fe(CN)_5NO]\cdot 3H_2O$	Orange-red	0.06 ± 0.03	1.70 ± 0.03	0.24, 0.26
$Mn[Fe(CN)_5NO]\cdot 2H_2O$	Yellowish	-0.02 ± 0.02	1.67 ± 0.03	0.24, 0.24
$Fe[Fe(CN)_5NO]\cdot 5H_2O$	Chocolate			
Low-spin Fe^{II}		-0.01 ± 0.02	1.74 ± 0.03	0.30, 0.28
High-spin Fe^{2+}		1.22 ± 0.03	2.75 ± 0.05	0.30, 0.28
$Co[Fe(CN)_5NO]\cdot 5H_2O$	Pink	-0.01 ± 0.03	1.72 ± 0.03	0.26, 0.24
$Ni[Fe(CN)_5NO]\cdot 5H_2O$	Gray-green	0.06 ± 0.02	1.89 ± 0.03	0.28, 0.28
$Cu[Fe(CN)_5NO]\cdot 2H_2O$	Light green	0.01 ± 0.02	1.75 ± 0.02	0.24, 0.30
$Zn[Fe(CN)_5NO]\cdot 2H_2O$	Buff	-0.02 ± 0.02	1.91 ± 0.02	0.24, 0.24
$Cd[Fe(CN)_5NO]\cdot 2H_2O$	Buff-white	-0.03 ± 0.02	1.72 ± 0.04	0.28, 0.26
$Fe[Mn(CN)_5NO]\cdot 2H_2O$	Dark green			
High-spin Fe^{2+}		1.24 ± 0.02	2.76 ± 0.03	0.22, 0.22

[a] All data have been converted relative to sodium pentacyanonitrosyl ferrate(II) dihydrate as the standard reference material by adding 0.48 mm/sec for the Cu source. Some authors also refer to it as differential isomer shift (δ_0).

equivalent quantities (0.01 mol) of the respective metal chlorides and sodium nitroprusside (eq 2) except in the case of ferrous nitroprusside where ferrous sulfate was used.

$$MCl_2 + Na_2[Fe(CN)_5NO] \longrightarrow M[Fe(CN)_5NO] + 2NaCl \quad (2)$$
$$(M = Mn, Co, Ni, Cu, Zn, Cd)$$

The pentacyanonitrosyls of manganese, $K_3[Mn(CN)_5NO]\cdot 2H_2O$ and $K_2[Mn(CN)_5NO]$, were prepared and purified as reported by Cotton, *et al.*[31] $Fe[Mn(CN)_5NO]\cdot 2H_2O$ was obtained as a dark green, shining, crystalline compound by adding an equivalent quantity of $FeSO_4\cdot 7H_2O$ to the freshly prepared $K_2[Mn(CN)_5NO]$ and washing the precipitate so obtained with acetone and chloroform.

The compounds gave satisfactory analyses for C, H, and N. In some cases metal estimations were also carried out using suitable gravimetric methods.

Mössbauer Spectra.—The Mössbauer spectra were recorded[24,26] using a constant-velocity mechanical drive (NSEC, Model B). The ^{57}Co source was obtained from BARC, Bombay, India, and was diffused into Cu foil (~1 mCi). The drive was precalibrated by recording spectra of standard iron and 310SS absorbers. The source and the absorber both were kept at room temperature. The spectral parameters and their errors were determined from the data as described earlier.[26] All lines were assumed to have Lorentzian shapes.

Infrared Spectra.—These were recorded with Perkin-Elmer infrared grating spectrophotometer, Model 521, using KBr pellets in the region 3000–300 cm^{-1}. The instrument was calibrated against the standard lines of indene, CO_2, and HCl as reported in the literature. The band positions reported here are within an accuracy of ±2 cm^{-1}.

X-Ray Spectra.—The X-ray diffractographs were recorded with a General Electric X-ray diffractometer using the Kα radiations of Fe.

Results

All the nitroprussides gave two-line spectra showing large quadrupole splittings except for $Fe[Fe(CN)_5NO]\cdot 5H_2O$, which consisted of four lines as shown in Figure 1. Various Mössbauer parameters calculated from the spectra are given in Table I. The isomer shift data, reported in Table I, have been calculated relative to the center of gravity of the sodium nitroprusside spectrum at room temperature. Our results of zinc nitroprusside agree well with those reported by Brady, Duncan, and Mok.[8]

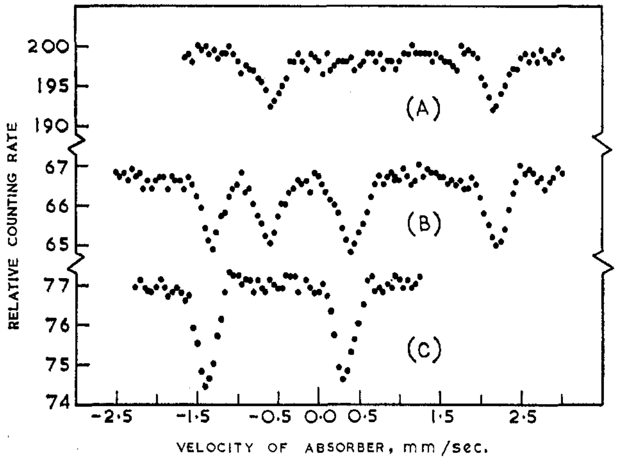

Figure 1.—Mössbauer spectra of (A) $Fe[Mn(CN)_5NO]\cdot 2H_2O$, (B) $Fe[Fe(CN)_5NO]\cdot 2H_2O$, and (C) $Mn[Fe(CN)_5NO]\cdot 5H_2O$.

The line widths (fwhm, full-width at half-maximum) listed in Table I are all almost the same within errors (0.22–0.33 mm/sec) as reported for other low-spin iron complexes. This indicates an absence of substantial broadening which would mean fast electronic relaxation rates.

Discussion

In the nitroprusside anion $Fe(CN)_5NO^{2-}$ the five cyanide (CN^-) and one nitrosyl (NO^+) ligands are covalently bonded around the iron atom, forming a distorted octahedral complex with d^2sp^3 hybridization where iron has a formal charge of 2+. In Figure 2 is shown a diagrammatic representation of the basic structural unit[11] of the nitroprusside anion in idealized C_{4v} symmetry as proposed by Manoharan and Hamilton.[32] The ligands NO and trans CN are approximately collinear with the central iron atom, which is displaced slightly in the direction of the NO group from the plane of the four pseudoequivalent CN groups (in the case of sodium nitroprusside this displacement is 0.2 Å). Due to the presence of strong ligand fields caused by the presence of CN^- and NO^+ ligands, all the nitroprussides under consideration are spin-paired,

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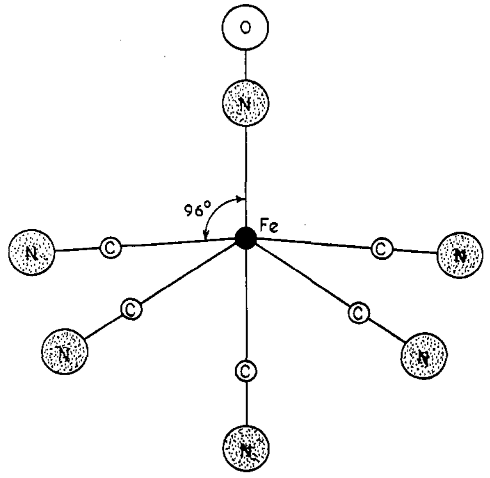

Figure 2.—Basic structural unit of the nitroprusside anion $Fe(CN)_5NO^{2-}$ in idealized C_{4v} symmetry.

covalent, and diamagnetic complexes. Here all the ligands remain linked to the central iron nucleus by σ bonds but strong $d_\pi \rightarrow p_\pi$ bonding has been suggested[21,22,33] due to back-donation of electrons from the filled metal d_π orbitals (d_{xz}, d_{yz}, and d_{xy}, also termed as e and b_2) to the empty ligand antibonding p_π orbitals. The ground state of iron in sodium nitroprusside has been determined to be $^1A_1$ with electronic configuration $(d_{xz}, d_{yz})^4(d_{xy})^2$. Manoharan and Gray[21] have calculated the energy separation between these two levels (e and b_2) as 4570 cm^{-1} which is caused by the replacement of one of the cyanide groups by a nitrosyl group. This is mainly responsible for generating an asymmetry at the iron nucleus and an increased back-donation. (It is also evident from the comparative bond distances Fe–N = 1.63 Å and Fe–C = 1.91 Å.) Manoharan and Gray[21] have also proposed that the electrons in the lower doublet (d_{xz}, d_{yz}) are strongly delocalized by back-donation to the 2p orbitals of the nitrosyl ligand whereas the d_{xy} electrons are slightly less delocalized to the equatorial cyanides. Thus the major contribution to the EFG comes from this asymmetric expansion of the e and b_2 electrons toward the ligand and a large quadrupole splitting is expected.

Crystal Structure.—The crystal structures of some of the nitroprussides have been reported. Manoharan and Hamilton[32] have shown, by single-crystal X-ray analysis, that $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ has an orthorhombic unit cell with four units and space group D_{2h}^{12}-P_{nnm}. In this compound ON–Fe–CN lies on the mirror plane with the nitroprusside anion having approximately C_{4v} symmetry. The powder patterns of other alkali metal nitroprussides of Li, K, Rb, Cs, NH_4, and Ag taken by us were found to have similar diffractographs. Salvadeo[30] has shown that nitroprussides of Fe, Co, and Ni have face-centered-cubic structures. Ayers[31] has examined nitroprussides of Cu(I) and Cu(II) which have primitive cubic structures. We recorded powder diffractographs of nitroprussides of Mn, Zn, and Cd and found them to be similar to those of the Ni and Co analogs. Hence it can be assumed that in all the nitroprussides, the basic unit of the nitroprusside anion, *i.e.*, $Fe(CN)_5NO^{2-}$, does not alter significantly. In the case of $Fe[Fe(CN)_5NO]\cdot 5H_2O$, however, there are two types of iron—one ionic and another covalently bonded. Recently Tullberg and Vannerberg[34] have shown that $K_3[Mn(CN)_5NO]\cdot 2H_2O$ (space group *Cc* with four units per unit cell) has the similar crystal structure as sodium nitroprusside, which means that the basic unit $Mn(CN)_5NO^{3-}$ is similar to that of $Fe(CN)_5NO^{2-}$ as shown in Figure 2. The esr studies of $Mn(CN)_5NO^{2-}$ doped in single crystals of $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ indicate that the $Mn(CN)_5NO^{2-}$ ion substitutes very well into the $Fe(CN)_5NO^{2-}$ units.[35] Therefore it is reasonable to assume that $K_2[Mn(CN)_5NO]$ and $Fe[Mn(CN)_5NO]\cdot 2H_2O$ will also have the same basic structural units.

Infrared Spectra.—In order to understand the effect of outer cations, we looked at the stretching modes of vibrations of N–O, C–N, Fe–N, and Fe–C bonds in various nitroprussides. The corresponding frequencies are tabulated in Table II. We have assigned these frequencies by comparing with the assignments made by Manoharan,[35,36] *et al.* As is clear from Table II, ν_{N-O} does not change substantially. Therefore, the percentage of π^* NO character for all cases can be taken to be around 22–26% on the basis of calculations done by Manoharan and Gray[36] for various nitrosyl compounds. It is to be noted that in most cases the other stretching frequencies also do not show any pronounced variations. These observations lend further support to our earlier assertion that in all the nitroprussides the basic structural unit remains the same. All the observed changes are presumably due to the influences of the outer cations.

TABLE II

INFRARED STRETCHING FREQUENCIES FOR VARIOUS NITROPRUSSIDES (IN CM^{-1})

Compd	C≡N	N═O	M—N	M—C
$Li_2[Fe(CN)_5NO]\cdot 3H_2O$	2147	1932	657, 638	435
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	2173	1939	661, 652	413
$(NH_4)_2[Fe(CN)_5NO]\cdot H_2O$	2136	1927	658, 641	402
$K_2[Fe(CN)_5NO]\cdot 2H_2O$	2134	1933	653	399
$Rb_2[Fe(CN)_5NO]$	2138	1925	657, 640	402
$Cs_2[Fe(CN)_5NO]$	2128	1932	653, 645	401
$Ag_2[Fe(CN)_5NO]$	2132	1933	657, 641	399
$Cu_2[Fe(CN)_5NO]\cdot 3H_2O$	2197	1934	653	435
$Mn[Fe(CN)_5NO]\cdot 2H_2O$	2168	1925	659, 642	428
$Fe[Fe(CN)_5NO]\cdot 5H_2O$	2178	1933	657	432
$Co[Fe(CN)_5NO]\cdot 5H_2O$	2163	1925	654, 638	427
$Ni[Fe(CN)_5NO]\cdot 5H_2O$	2183, 2142	1937	657	442
$Cu[Fe(CN)_5NO]\cdot 2H_2O$	2193	1948	657, 638	427
$Zn[Fe(CN)_5NO]\cdot 2H_2O$	2172	1934	658	432, 410
$Cd[Fe(CN)_5NO]\cdot 2H_2O$	2168	1942	661, 644	429, 418
$Ba[Fe(CN)_5NO]\cdot 7H_2O$	2138, 2023	1922	582	. . .
$K_3[Mn(CN)_5NO]\cdot 2H_2O$	2128, 2087	1732	668	448
$K_2[Mn(CN)_5NO]$	2168, 2107	1886	. . .	422
$Fe[Mn(CN)_5NO]\cdot 2H_2O$	2119	1802	. . .	. . .

In the case of the manganese pentacyanonitrosyl complex $K_3[Mn(CN)_5NO]\cdot 2H_2O$ all the frequencies agree well with reported assignments made by Cotton, *et al.*[31] For $Fe[Mn(CN)_5NO]\cdot 2H_2O$ the assignments have been done based on the studies[31] of $Zn[Mn(CN)_5NO]\cdot 2H_2O$.

Isomer Shift.—The values of isomer shift for both of the series of nitroprussides listed in Table I are characteristic of low-spin iron(II) compounds and indicate

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very small variations with the change in outer cation. No unambiguous correlation could be observed between the isomer shift and the electronegativity of the cations.

Quadrupole Splitting.—All nitroprussides showed a symmetric doublet (except ferrous nitroprusside) with large quadrupole splittings (ΔE_Q = 1.50–2.00 mm/sec) which are comparable to those observed for high-spin Fe^{2+} compounds.[37] Quadrupole splitting in a series of compounds of similar geometry can be influenced by a number of factors, the most obvious of these being (i) electronegativity[38] of the cation, (ii) size of the cation,[26] and (iii) the lability of the electrons in the d orbitals of the cations. Since we are investigating the influence of an outer cation on an already existing large asymmetry, the variations due to the changes in the above parameters are, in general, not too large. We did not see any pronounced and systematic variation in the quadrupole splitting of any of the above factors.

Ferrous Nitroprusside.—The Mössbauer spectrum of ferrous nitroprusside consists of four well-resolved lines of almost equal intensity as shown in Figure 1. An analysis of this spectrum reveals that two of the lines correspond to the usual nitroprusside part of the compound and yield a quadrupole splitting, ΔE_Q, of 1.74 ± 0.03 mm/sec and an isomer shift, δ, of −0.01 ± 0.02 mm/sec. The remaining two lines would then give ΔE_Q = 2.75 ± 0.05 mm/sec and δ = 1.22 ± 0.03 mm/sec. These parameters correspond[37] to the high-spin state of Fe^{2+}. To confirm this we synthesized and studied $Fe[Mn(CN)_5NO]\cdot 2H_2O$ where the inner unit of nitroprusside anion is structurally the same but does not contain iron and the outer iron is present as such. This compound gave rise to only a two-line spectrum depicting the high-spin state of Fe^{2+}, with the Mössbauer parameters δ = 1.24 ± 0.02 mm/sec and ΔE_Q = 2.76 ± 0.02 mm/sec. These agree well with those assumed for the high-spin state in the case of ferrous nitroprusside. Therefore we can infer that there are two clearly defined states of iron, *i.e.*, (i) the inner iron in the usual low-spin state and covalently bonded with five CN^- and one NO^+ groups and (ii) the outer cationic iron in the high-spin state. This is a confirmation of the results of magnetic susceptibility measurements.[30]

Recently Fung and Drickamer[39] have also studied $Fe[Fe(CN)_5NO]$ and confirmed the presence of two types of irons by tagging them with ^{57}Fe separately. Our results are comparable with these within experimental error. These authors have also found that the percentage of high-spin iron increases with the increase in pressure.

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Electronic Spectra of Ruthenium(III) and Osmium(III) in Chloride Melts

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Ruthenium(III) adopts octahedral coordination in LiCl–KCl at 450° with the ligand field parameters Δ = 18.7, B = 0.49 and C = 2.3 kK. A preliminary study of osmium(III) chloride shows that it disproportionates to Os(IV) and Os metal in both LiCl–KCl and $BiCl_3$, the rate of decomposition rising markedly above 500°. However, the coordination of Os(III) appears to be distorted octahedral with a trigonal or tetragonal ligand field component of 4.0 kK and a spin-orbital coupling constant of 2.7 kK. Ruthenium(III), osmium(III), and osmium(IV) showed no electrochemical activity in LiCl–KCl.

The ligand field spectra of complexes of Ru(III) and Os(III) have not been studied in great detail. For example, Jørgensen[1,2] measured the spectrum of $RuCl_6^{3-}$ in hydrochloric acid but made no definite assignments, and Johnson and Dickinson[3] noted the presence of a weak band at 17.5 kK and a shoulder at 24.5 kK for $RuCl_3$ dissolved in LiCl–KCl eutectic melt. The spectrum of $Ru(ox)_3^{3-}$ (ox = oxalate) has been given and interpreted.[4] Again, Jørgensen[2] has reported the charge-transfer spectrum of $OsCl_6^{3-}$ in hydrochloric acid but no ligand field bands were observed. On the other hand, ligand field bands of the Os(III) complexes $Os(acac)_3$ and $OsCl_3(Sb(C_6H_5))_3$ have been assigned.[5,6]

In this paper we present further measurements of the spectrum of Ru(III) in LiCl–KCl and the first datum concerning Os(III) in both LiCl–KCl and $BiCl_3$. It transpires that Os(III) is in equilibrium with Os(IV) and Os metal in these melts but some useful information may be extracted from the spectra.

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