Unusual Quadrupole Splitting in Di- and Trialkylamine Substituted Pentacyanoferrate(II) Complexes

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A series of pentacyanoferrate complexes, Na₃[Fe(CN)₅L]·nH₂O, where L = (CH₃)₂NH, (C₆H₅)₂NH, (C₆H₅)₃N, (C₂H₅)₂NH, (C₄H₉)₂NH, and (C₆H₅)₂NH were studied by Mössbauer and infrared spectroscopy. All the complexes exhibited two line spectra with DEq = 0.73–1.92 ms⁻¹ and δ = −0.04–0.49 ms⁻¹ (w.r.t. SNP) and can be divided into two groups with well defined parameters. Partial isomer shift and partial quadrupole splitting values were correlated with bonding characteristics.

1. Introduction

In pentacyanoferrates(II), [Fe(CN)₅L]⁻ if L is a weak field ligand such as NH₃ which can coordinate through σ-bonding only without any possibility of π-back donation, strong asymmetry is generated at the iron nucleus. Such type of complexes were known since the early part of this century [1, 2]. The Mössbauer spectrum of Na₃[Fe(CN)₅NH₃]·H₂O was first reported by Fluck et al. [3]. Several workers have reported their studies with L = NO₂⁻, SO₃⁻, Py, P(C₆H₅)₃, H₂O etc. and correlated their results [3–13]. Some workers have studied unusual pentacyanoferrate(II) complexes where metal ligand charge transfer (MLCT) band positions have been correlated with δ and DEq values [12–14]. Recently, Rasmussen and Meyers [15] have suggested transfer of charge in such type of complexes. In this communications we report our results on some Na₃[Fe(CN)₅L]·nH₂O complexes where L is a dialky- or trialkylamine. An unusually high quadrupole splitting is observed in some cases which are also characterized by low δ values. This has been explained due to possible changes in bonding characteristics of di- and trialkylamines with substitution of bulky groups. Infrared data also support this conclusion.

2. Experimental

The complexes were prepared by mixing an aqueous solution of sodium nitroprusside with the corresponding amine (L) solution and sodium acetate as described in the literature [2, 10]. The mixture was stirred thoroughly and an excess of amine was added until the solution gave a negative test for nitroprusside. Precipitation of the complexes was effected by the addition of cold absolute alcohol. The complexes were dried in vacuo over fused CaCl₂. The complexes were characterized by the analysis of C, H, N, and Fe contents which agreed well with the proposed molecular formula. The complexes are unstable over prolonged standing and hence all measurements are to be taken within a week.

Mössbauer spectra were recorded on a transducer driven spectrometer in constant velocity mode (ECIL, Hyderabad) at room temperature. A ~5 mCi ⁵⁷Co(Rh) source (Amersham International, UK) was used. The spectrometer was calibrated using natural iron foil, and sodium nitroprusside dihydrate (SNP) was used as standard. Spectral lines were assumed to have Lorentzian line shape and the Mössbauer parameters were calculated from visual fitting. Infrared spectra (4000–400 cm⁻¹) were recorded on a SPECORD 75 IR spectrophotometer in Nujol medium.

3. Results

The Mössbauer spectra of all the complexes exhibit a quadrupole doublet at room temperature with DEq = 0.73–1.92 ms⁻¹ and δ = −0.04–0.49 ms⁻¹ (w.r.t. SNP). The Mössbauer parameters of the individual complexes are listed in Table I. Also given in the Table are partial isomer shift (p.i.s.) and partial quadrupole splitting (p.q.s.) values for the substituted amine ligands and characteristic infrared frequencies for C≡N stretching and Fe–C≡N bending vibrations. Typical Mössbauer spectra of dimethyl- and diphenylamine substituted complexes are shown in Fig. 1.
Table I. Mössbauer parameters and characteristic IR frequencies in pentacyanoferate(II) complexes, 
Na₃[Fe(CN)₅L]·nH₂O.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Isomer shift [δ] [mms⁻¹]</th>
<th>Quadrupole splitting [ΔE₀] [mms⁻¹]</th>
<th>Partial isomer shift [p.i.s.] [mms⁻¹]</th>
<th>Partial quadrupole splitting [p.q.s.] [cm⁻¹]</th>
<th>νCN [cm⁻¹]</th>
<th>δ_{Fe-C=N}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₃[Fe(CN)₅NH(CH₃)₂]·2H₂O</td>
<td>0.49±0.03</td>
<td>0.73±0.03</td>
<td>0.28</td>
<td>-0.48</td>
<td>2020 m</td>
<td>550 w</td>
</tr>
<tr>
<td>Na₃[Fe(CN)₅NH(C₂H₅)₂]·2H₂O</td>
<td>0.40±0.03</td>
<td>0.86±0.02</td>
<td>0.19</td>
<td>-0.41</td>
<td>2030 s</td>
<td>550 b</td>
</tr>
<tr>
<td>Na₃[Fe(CN)₅N(C₂H₅)₂]·2H₂O</td>
<td>0.03±0.04</td>
<td>1.77±0.03</td>
<td>-0.18</td>
<td>0.05</td>
<td>2140 s</td>
<td>640 m</td>
</tr>
<tr>
<td>Na₃[Fe(CN)₅NH(C₃H₇)₂]·3H₂O</td>
<td>0.35±0.03</td>
<td>0.85±0.04</td>
<td>0.14</td>
<td>-0.42</td>
<td>2010 s</td>
<td>570 m</td>
</tr>
<tr>
<td>Na₃[Fe(CN)₅NH(C₄H₉)₂]·2H₂O</td>
<td>-0.04±0.04</td>
<td>1.82±0.03</td>
<td>-0.25</td>
<td>0.07</td>
<td>2140 m</td>
<td>640 w</td>
</tr>
<tr>
<td>Na₃[Fe(CN)₅N(C₄H₉)₃]·H₂O</td>
<td>0.05±0.03</td>
<td>1.92±0.04</td>
<td>-0.16</td>
<td>0.12</td>
<td>2140 s</td>
<td>650 m</td>
</tr>
<tr>
<td>Na₃[Fe(CN)₅NH(C₆H₅)₂]·2H₂O</td>
<td>0.02±0.03</td>
<td>1.75±0.03</td>
<td>-0.19</td>
<td>0.04</td>
<td>2130 m</td>
<td>640 w</td>
</tr>
</tbody>
</table>

* w.r.t. sodium nitroprusside dihydrate as standard; s = strong, m = medium, w = weak, b = broad.

4. Discussion

In complexes of the type [Fe(CN)₅L]³⁻, the central Fe atom is surrounded by five CN⁻ and an odd ligand (NHR₂ and NR₃ in the present study) in octahedral geometry. The electronic configuration will be t₂⁰g and the complexes are expected to be diamagnetic. But the electrons may be distributed asymmetrically as in the case of nitroprussides. Due to the odd ligand in the sixth position, symmetry is lowered from O₆ to approximately C₄v, and t₂⁰g orbitals are further split into d₁₇ and d₁₈ (also called e and b₂) [12]. While five CN⁻ ligands have pₓ orbitals available for back bonding, no such orbitals are available in the case of amines. Fluck [16] has indicated more or less comparable π-bonding ability for NH₃ and NO₂⁻ ligands while Danon [17] has assumed greater π-bonding ability for NO₂⁻. Manoharan et al. [18] have studied several hexanitroferrates and confirmed π-bonding ability of NO₂⁻ but found it to be much less than that of CN⁻ ligands. Therefore, in the case of five CN⁻ and an amine ligand, it may be possible that the central Fe atom is slightly pushed towards trans CN⁻ due to its greater π-bonding ability as in the case of sodium nitroprusside [19], where it is shifted towards NO.

4.1 Quadrupole splitting

We have observed large quadrupole splittings, ΔE₀ = 0.73–1.92 mm s⁻¹, in all complexes. On the basis of the ΔE₀ values, complexes can be divided into two well defined groups (hereafter named as Gr. I and II). Group I comprises of dialkylamine substituents viz. (CH₃)₂NH, (C₂H₅)₂NH and (C₃H₇)₂NH exhibiting ΔE₀ values ~ 0.80 mm s⁻¹ which are almost equal to that observed for monoalkylamine substituted complexes [6–11]. In group II are the trialkylamines [(C₂H₅)₃N and (C₄H₉)₃N] and the bulky dialkylamines [(C₃H₇)₂NH and (C₆H₅)₂NH], their complexes exhibiting ΔE₀ values ~ 1.80 mm s⁻¹ which is more than double that observed for group I complexes. Isomer shift values of these complexes also vary in a wide range, ~0.04–0.49 mm s⁻¹ (w.r.t. SNP), which are well within the typical range for iron(II) low spin complexes [3, 17, 20]. Interestingly, δ values can also be divided into two well defined groups.
higher for Gr. I and lower for Gr. II complexes. However, no such large scale variation in $\delta$ and $\Delta E_O$ values was observed in monoalkylamine or phosphine substituted pentacyanoferrate(II) complexes [6-10, 12]. Therefore, it seems quite possible that some large scale change in bonding characteristics might be taking place in going from simple monoalkylamines and dialkylamines to bulky dialkylamines and trialkylamines. This change in bonding characteristics may, in turn, be forcing large distortions in geometry so as to more than double $\Delta E_O$ and lower $\delta$ values. One possible explanation for this unusual observations may be that trialkylamines $[(C_3H_5)_3N$ and $(C_4H_9)_3N]$ and bulky dialkylamines $[(C_4H_9)_2NH$ and $(C_6H_5)_2NH]$ might be forcing $d_y$ orbitals of the central iron atom to go out of plane of four CN" ligands leading to increased $\pi$-bonding with trans CN" ligands as in the case of sodium nitroprusside [21]. This is in accordance with a suggestion of Ballhausen and Gray that in MX₅L type of complexes all $\pi$-bonding is axially directed while planar $\pi$-orbitals remain non-bonding [22].

During the last one and a half decade several workers have attempted to correlate $\delta$ and $\Delta E_O$ values and to use this correlation in predicting the sign of EFG [20, 23-26]. A linear correlation has been observed for all $[Fe(CN)_5L]^-$ type of complexes with varying substituents indicating a decrease in $\Delta E_O$ with increasing $\delta$ [26, 27]. A positive sign of EFG has been predicted for Gr. II and negative for Gr. I complexes [26, 27]. However, a confirmation for this fact is yet to be obtained from magnetic perturbation studies.

### 4.2 Partial isomer shift and quadrupole splitting

Several attempts have been made to evaluate partial isomer shift (p.i.s.) and partial quadrupole splitting (p.q.s.) values of the ligands in a series of isostructural complexes and correlating them with bonding characteristics [20, 28, 29]. The p.i.s. and p.q.s. values for the new substituted amine ligands were calculated using the following equations;

$$[L]_{\text{p.i.s.}} = \delta - 0.21$$
$$[L]_{\text{p.q.s.}} = \frac{1}{2} (\Delta E_O - 1.68)$$

where $\delta$ and $\Delta E_O$ are observed values. These are listed in Table I. Plots of p.q.s. vs. $\delta$ and with p.i.s. are shown in Fig. 2. In both cases p.q.s. values increase with decreasing $\delta$ or p.i.s. values. For a distorted octahedral complex of the type $[Fe(CN)_5L]^- \text{it is }$ observed that $\delta$ values are affected whether L is a better $\sigma$-donor or $\pi$-acceptor than CN" trans to it [12, 15, 20]. In the present study where all the ligands are substituted amines, their $\sigma$-donor capacity is affected with alkyl or aryl group substitution. It could also be correlated with the change in base strength of di- and trialkylamines. It has been known that primary and secondary amines are better $\sigma$-donors whereas bulky dialkylamines and trialkylamines are poor $\sigma$-donors because
of hyperconjugation effects [30]. Similarly, diphenylamine is a weaker base than \( \text{NH}_3 \).