

## Proper and Improper Hydrogen Bonds in Metalloorganic Crystal Architecture: Experimental Evidence in $[\text{CoCp}_2]^+$ and $[\text{FeCp}_2]^+$ Salts

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The widely known hydrogen bond  $\text{X}-\text{H}\cdots\text{Y}$  between a proton donor  $\text{X}-\text{H}$  and a proton acceptor  $\text{Y}$  commonly gives rise to a lengthening of the  $\text{X}-\text{H}$  bond with a consequent low energy shift ("red shift") of the  $\nu(\text{X}-\text{H})$  frequency.<sup>1a,b</sup> Recently, great attention has been given to the so-called "improper hydrogen bond", which is characterized by a strengthening of the  $\text{X}-\text{H}$  bond together with an obvious high-energy shift ("blue shift") of the  $\nu(\text{X}-\text{H})$  frequency. There has been considerable theoretical work on the interpretation of the improper bond;<sup>2</sup> compared with the number of theoretical studies, the experimental data are rather scarce and mainly concern proton donors with  $\text{C}-\text{H}$  bonds and proton acceptors such as  $\pi$ -systems<sup>3</sup> or oxygen lone pairs.<sup>4</sup>

The present communication reports the first experimental example where the same metalloorganic species shows both the proper and improper effects by interacting with different proton acceptors. The metallocinium salts are a potential source of the improper H bond, for they may be associated with a variety of the possible anions and a  $\text{C}-\text{H}\cdots\text{X}$  bond is a fundamental motif of the crystal architecture.<sup>5</sup> The measurement of the  $\nu(\text{C}-\text{H})$  shift is the best, and perhaps the unique, experimental evidence; the bond length variation is predicted to be much lower than the experimental standard deviation.<sup>2d,e</sup>

The vibrational pattern of metallocene complexes in the  $\text{C}-\text{H}$  stretching region is well documented.<sup>6</sup> The solution infrared and Raman spectra are dominated by the highest-frequency  $e_{1u}$  and  $a_{1g}$  modes, respectively.<sup>6a,b</sup> Notwithstanding the possible effect of the intermolecular coupling and of the reduced symmetry in the crystals, the spectral pattern in the solid state does not show significant differences from the solution data;<sup>6c,d</sup> occasionally, a small splitting of the degenerate modes is observed. This behavior may equally well arise from a variety of different interactions between the  $\text{C}-\text{H}$  bonds and the anion. It is unlikely that for all the complexes each  $\text{C}-\text{H}$  bond is engaged in an identical interaction with the anion.<sup>7</sup> However, the spectral pattern indicates that the possible different effects are averaged over all the H atoms of the Cp ring. Thus, it is reasonable to consider the two dominant infrared and Raman bands as pseudo " $e_{1u}$ " and " $a_{1g}$ "  $\nu(\text{CH})$  modes, respectively. Significantly, their frequencies are anion dependent, as reported in Table 1. The obvious reference data are the corresponding spectra in solution. By using solvents such as  $\text{CH}_3\text{CN}$ , which minimize any cation-anion interferences,<sup>8</sup> very similar infrared spectra have been obtained. The average values of the  $e_{1u}$  frequency ( $3110 \pm 1 \text{ cm}^{-1}$  for  $[\text{FeCp}_2]^+$  salts and  $3115 \pm 1 \text{ cm}^{-1}$  for  $[\text{CoCp}_2]^+$  salts) have been taken as the reference frequency; that is, the  $\nu(\text{C}-\text{H})$  without any H-bond interaction.<sup>9</sup> The value of  $\Delta\nu$  ( $\nu(\text{solid state}) - \nu(\text{solution})$ ) indicates complexes having a proper H bond (red shift,  $-\Delta\nu$ ) and those with an improper H bond (blue shift,  $+\Delta\nu$ ).

Table 1<sup>a</sup>

cation	anion	$"a_{1g}" (\text{cm}^{-1})$		$"e_{1u}" (\text{cm}^{-1})$	
		Raman	$\Delta\nu$	infrared	$\Delta\nu$
$[\text{FeCp}_2]^+$	$[\text{PF}_6]^-$	3130	+10	3124	+14
	$[\text{BF}_4]^-$	3126	+6	3103	-7
	$[\text{FeCl}_4]^-$	3116	-6	3102	-8
	$[\text{SbCl}_4]^-$	3114	-4	3103	-7
	$[\text{I}_3]^-$	3098	-22	3090	-20
$[\text{CoCp}_2]^+$	$[\text{Co}(\text{CN})_6]^{3-}$	3135	+11	3128 av	+13 av
	$[\text{PF}_6]^-$	3134	+10	3128	+13
	$[\text{Co}(\text{CO})_4]^-$	3128	+4	3119	+4
	$[\text{Br}_3]^-$	3110	-14	3100	-15
	$[\text{I}]^-$	3059	-65	3057	-58

<sup>a</sup> These data are shown more clearly by the selected spectra illustrated in Figure 1.

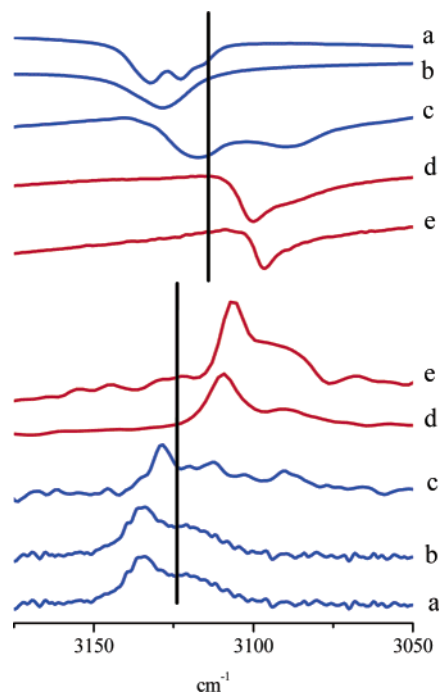


Figure 1. Infrared (upper) and Raman (lower) spectra of the  $[\text{Cp}_2\text{Co}^+]$  salts in solid state. The vertical bars correspond to the average  $e_{1u}$  and  $a_{1g}$  mode frequencies in solution, respectively. The blue spectra indicate the presence of an improper H-bond (a:  $[\text{Co}(\text{CN})_6]^{3-}$ , b:  $[\text{PF}_6]^-$ , c:  $[\text{Co}(\text{CO})_4]^-$ ), and red spectra, the proper H-bond (d:  $[\text{Br}_3]^-$ , e:  $[\text{I}]^-$ ).

Raman spectra should, in principle, be preferred as an experimental test both because the  $a_{1g}$  mode refers to the in-phase displacement of all the  $\text{C}-\text{H}$  vibrators and the solid state Raman pattern is stronger than the infrared (see Figure 1). Unfortunately, the solutions usually give rise to a very low scattering. We were able to obtain good Raman spectra of  $[\text{FeCp}_2]_3$  and of  $[\text{CoCp}_2]_3$  dissolved in

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MeCN, and they have  $a_{1g}$  frequencies of 3120 and 3124  $\text{cm}^{-1}$ , respectively. Taking this value as a reference for  $[\text{CoCp}_2]^+$  and  $[\text{FeCp}_2]^+$  salts, the blue/red shift of the  $a_{1g}$  mode is easily calculated (Table 1).

In some cases the effect of the hydrogen bond was also shown by the vibrational pattern of the anions. For instance, the typical vibrational modes of  $[\text{PF}_6]^-$ ,  $[\text{BF}_4]^-$ , and  $[\text{Co}(\text{CO})_4]^-$  are shifted to longer wavelengths as a consequence of the weakening of the P–F, B–F, and C–O bonds.<sup>10</sup> The same effect is evident in the complex  $[\text{CoCp}_2]_3^+[\text{Co}(\text{CN})_6]^{3-}$ . In this case, however, the C–H $\cdots$ NC interaction increases the CN stretching frequency (the  $\nu(\text{CN})_{t_{1u}}$  is shifted from 2129  $\text{cm}^{-1}$  in  $\text{K}_3[\text{Co}(\text{CN})_6]$  to 2158  $\text{cm}^{-1}$ ) as is often found when moving from terminal to bridging CN.<sup>11</sup>

Two interpretations have been proposed to explain the physical basis of the improper H-bond. One considers the improper bond as basically different from the proper bond, in that for the former a two-step mechanism is proposed, implying a charge transfer from the proton acceptor to a remote part of the proton donor, followed by a structural reorganization of the proton donor itself.<sup>2a</sup> The other interpretation considers the two bonds very similar in nature, focusing attention on the quantitative difference between the various interactions.<sup>2c–g</sup> We are aware that a reliable interpretation of the examples we presented can be offered only by performing relevant quantum chemical calculations. Nevertheless, the second interpretation appears the most reasonable, as all the C–H bonds participate in the interaction with the proton acceptor, so that the entire  $\text{C}_5\text{H}_5$  unit acts as proton donor, and a “remote part” which accepts charge density cannot be evidenced.

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**Supporting Information Available:** Infrared spectra of different  $[\text{CoCp}_2]^+$  salts in acetonitrile and acetone (Figure S1). This material is available free of charge via the Internet at <http://www.pubs.acs.org>.

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- (9) The solubility of the salts and the spectral background of the solvents strongly limit the choice available. The best solvents ( $\text{CH}_3\text{CN}$  or acetone) are presumably noninnocent with respect to H-bonding. However, their effects are both very similar and very small, as illustrated in Figure S1 of the Supporting Information, which shows spectra for some  $[\text{Cp}_2\text{Co}]^+$  salts in  $\text{CH}_3\text{CN}$  or acetone. The frequency values of the  $e_{1u}$  mode fall in the range  $3114 \pm 4 \text{ cm}^{-1}$ .
- (10) The  $\nu(\text{P–F})_{a_{1g}}$  is 740  $\text{cm}^{-1}$  in the metallocinium complexes and 752  $\text{cm}^{-1}$  in  $[\text{K}]^+[\text{PF}_6]^-$ ; the  $\nu(\text{B–F})_{a_1}$  is 762  $\text{cm}^{-1}$  in  $[\text{Cp}_2\text{Fe}]^+[\text{BF}_4]^-$  and 772  $\text{cm}^{-1}$  in  $[\text{K}]^+[\text{BF}_4]^-$ ; the  $\nu(\text{CO})_{a_1}$  is 2007  $\text{cm}^{-1}$  in  $[\text{Cp}_2\text{Co}]^+[\text{Co}(\text{CO})_4]^-$  and 2025  $\text{cm}^{-1}$  in  $[\text{Na}]^+[\text{Co}(\text{CO})_4]^-$ .
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