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Mössbauer and Spectroscopic Properties of Binuclear Iron and Ruthenium Pyrazine Bridged Complexes

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Binuclear pyrazine bridged complexes of ruthenium and iron have been investigated by many authors [1–4].

Spectroscopic studies of $[(NH_3)_5Ru–pyz–Fe(CN)_5]$ reported by Haim *et al.* [4] and by Toma and Santos [3], as well as those carried out by Felix and Ludi on $[(CN)_5Fe–pyz–Fe(CN)_5]^{5-}$ [2], have shown that these mixed-valence systems of trapped-valence type have localized electronic states Ru(III), Fe(III) and Fe(II). Because of the divergences in the spectroscopic data reported by different authors [3, 4], we decided to re-examine those compounds and to complete the available data with results obtained from Mössbauer spectroscopy.

Experimental

Preparation of Complexes

$[Ru(NH_3)_5pyz](ClO_4)_2$ [1] and $Na_3[Fe(CN)_5pyz]\cdot 3H_2O$ [5] were prepared according to the cited literature methods. The complexes $Na[(NH_3)_5Ru–pyz–Fe(CN)_5]\cdot 2H_2O$ and $[(NH_3)_5Ru–pyz–Fe(CN)_5]xH_2O$ were obtained by literature methods [4]. *Anal.* Calcd. for $Na[(NH_3)_5Ru–NC_4H_4N–Fe(CN)_5]\cdot 2H_2O$: Ru, 19.8; Fe, 10.9; C, 21.1; H, 4.5; N, 32.9. Found: Ru, 19.3; Fe, 10.6; C, 21.0; H, 4.4; N, 32.6. Calcd. for $[(NH_3)_5Ru–NC_4H_4N–Fe(CN)_5]$: Ru, 21.4; Fe, 11.9; C, 23.0; H, 4.5; N, 35.7. Found: Ru, 21.0; Fe, 11.4; C, 22.9; H, 4.5; N, 35.1. Methods reported by Ludi *et al.* [2] were used to prepare $Na_6[(CN)_5Fe–pyz–Fe(CN)_5]\cdot 8H_2O$ and $Na_5[(CN)_5Fe–pyz–Fe(CN)_5]\cdot xH_2O$. *Anal.* calcd. for $Na_6[(CN)_5Fe–NC_4H_4N–Fe(CN)_5]\cdot 8H_2O$: Fe, 15.2; C, 22.9; N, 22.9; H, 2.7. Found: Fe, 14.9; C, 22.2; N, 22.1; H, 3.0. The analyses were not satisfactory because of the hygroscopic properties of this complex. Purity of the product was tested by ^{1}HNMR and Mössbauer spectroscopy. $Na_5[(CN)_5Fe–NC_4H_4N–Fe(CN)_5]\cdot xH_2O$ was extremely hygroscopic and decomposed in solid state; thus Fe, C, N and H analysis were not satisfactory (see text).

Analytical methods

C, H, N were carried out by the microanalytical laboratory in the Institute of Chemistry of Wrocław University. Iron [6] and ruthenium [7] were determined spectrophotometrically following decomposition as described by Haim *et al.* [4]. Electronic absorption spectra in KBr pellets, aqueous solution and diffuse reflectance spectra in magnesium oxide were measured with a Beckman 5240. IR spectra in KBr pellets were recorded with a Perkin-Elmer 180 Spectrophotometer.

Mössbauer spectra were measured by method described previously [8]. All syntheses and measurements, repeated several times, gave reproducible results.

Results and Discussion

I. Compounds of Fe–pyz–Ru Type

The results obtained from electronic spectroscopy for compounds having a Ru–pyz–Fe core are in agreement with those reported by Haim *et al.* [4]. In the diffuse reflectance and absorption spectra in KBr of the mononuclear compound $[Ru(NH_3)_5pyz](ClO_4)_2$ a shoulder was observed at 600 nm which does not appear in the aqueous solution of that complex. In this region a $d \rightarrow \pi^*$ band of the protonized pyrazine was observed [9]. Since the intensity ratio of the 474 and 600 nm bands varies for samples obtained from different syntheses, it may be concluded that the long-wave band is due to the partially protonized ligand in the investigated compound in solid state.

The bathochromatic shift of the $d \rightarrow \pi^*$ band observed for the binuclear compound Ru(II)–pyz–Fe(II), in comparison with those of both the mononuclear compounds as well as a further bathochromatic shift of that band observed for the product of the one electron oxidation of the binuclear compound, is consistent with the results of Haim *et al.* [4].

According to the Taube–Creutz MO model [1], those variations in the position of the $d \rightarrow \pi^*$ band classify mixed-valence compounds to the trapped-valence group or to the class II according to the classification of Robin and Day [10]. The analysis of electronic spectra of a series of Ru–pyz–M and Fe–pyz–M compounds (where M = Rh(III) and Co(III)) accomplished by Haim *et al.* [4] suggested that in the one electron oxidation process the ruthenium centrum was oxidized. Haim's *et al.* [4] observations concerning the $\nu_{C–N}$ and σ_{NH_3} bands, which are in agreement with our results, are strongly in support of that conclusion.

For the mixed-valence complexes the appearance of an inter-valence band is expected. The 1370 nm band, reported also by other authors [3, 4], could be attributed to this transition. However Haim *et al.* [4]

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TABLE I. Mössbauer Parameters of the Complexes under Investigation (IS relative to SNP at 290 K).

Compound	Temp. [K]	IS [mm/s]	QS [mm/s]	Γ_- [mm/s]	Γ_+ [mm/s]
$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$	290	0.270	0.651	0.225	0.222
$Na_3[Fe(CN)_5pyz]\cdot 3H_2O$	290	0.264	0.921	0.249	0.245
$Na_6[(CN)_5FepyzFe(CN)_5]\cdot 8H_2O$	290	0.275	0.872	0.281	0.280
$Na_5[(CN)_5FepyzFe(CN)_5]\cdot xH_2O$	290	0.185 0.261	1.813 0.891		
$Na[(CN)_5FepyzRu(NH_3)_5]\cdot 2H_2O$	290	0.265	0.852	0.253	0.254
	80	0.329	0.847	0.390	0.381
$[(CN)_5FepyzRu(NH_3)_5]$	290	0.201	0.995	0.274	0.386
	80	0.283	1.123	0.460	0.428

have shown that the appearence of the band and its position are independent of the bridged monocores and of the bridging ligand, and that for some compounds it appears after aging. This suggests that the 1370 nm band should be attributed to the decomposition products.

In order to determine the electronic structures of the tested compounds and the interactions of the bridged core, Mössbauer spectra have been recorded (Table I, Fig. 1).

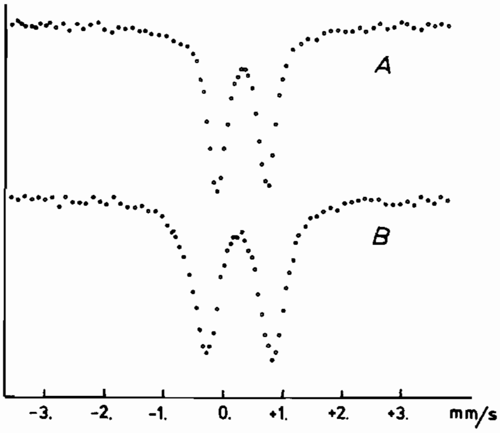

Fig. 1. Mössbauer spectra at 80 K: A, $Na[(CN)_5Fe-pyz-Ru(NH_3)_5]\cdot 2H_2O$; B, $[(CN)_5Fe-pyz-Ru(NH_3)_5]$.

The Mössbauer spectra of the mononuclear compound $Na_3[Fe(CN)_5pyz]\cdot 3H_2O$ and of the binuclear one having a Ru(II)–pyz–Fe(II) core are characterized by a well-shaped quadrupole doublet of very narrow resonance lines. For both the compounds, the magnitude of the isomeric shift (IS) compared with the SNP and the magnitude of the quadrupole splitting (QS) are typical of the Fe(II) ion surrounded by a distorted octahedron. From the absence of differences in the IS value and the small variations in QS due to variations in symmetry on going from the monomer to the dimer, we are led to conclude that the Fe(II) ion does not 'see' the difference between the sixths ligands: pyz, $[Ru(NH_3)_5pyz]^{2+}$ or $[Fe(CN)_5pyz]^{3-}$. This is consistent with Fleming's observations [11] where the replacement of σ-donor ligands by π-acceptor ones in the sixth coordination position of $[Fe(CN)_5]^{3-}$ does not affect the IS parameter. The constant electronic density on the iron nucleus results from interactions between the CN groups and the sixth ligand L. An increase in π-acceptor properties of L is accompanied by a decrease in the π-acceptor forces and increase in the σ-donor interactions of the cyanide groups. Those conclusions are strongly supported by the analysis of ^{13}CNMR spectra of the cyanide group and L ligand carbons for this series of compounds [12].

The Mössbauer spectrum of the product of one electron oxidation of the system Fe(II)–pyz–Ru(II) consists, as before, of a single quadrupole doublet with a QS value increased by about 0.1 mm s^{-1} and with a significantly lowered IS value. This change in the IS value is due to the increased density of s electrons on the iron ion. The density increase is caused by a shift of the d electron density towards the π-accepting Ru(III) ion, which results in a deshielding of the s electrons.

Nevertheless, the IS and QS parameter values are still typical of the ferrous ion. This fact supports the conclusions obtained from the analysis of the electronic and vibration spectra concerning the trapped-valence type of the studied mixed-valence compound and the localized electronic states Ru(III) and Fe(II).

In order to gain more detailed insight into this problem, Mössbauer spectra of Fe(II)–pyz–Ru(II) and Fe(II)–pyz–Ru(III) were recorded at the liquid nitrogen temperature. The observed variations of IS and QS resulted only from the second order Doppler effect. However, a considerable broadening of the resonance lines was observed, particularly for Fe(II)–pyz–Ru(III). This effect must be caused by a change in the mechanism and velocity of the electron density shift from Fe(II) toward Ru(III), the velocity decreasing to the order of 10^{-7} s (resolution time of

TABLE II. Mössbauer Parameters of the Complexes under Investigation. IS Relative to SNP at 290 K.

Compound No.	Temp. [K]	IS [mm/s]	QS [mm/s]	Γ_- [mm/s]	Γ_+ [mm/s]
II	290	0.270	0.651	0.225	0.222
III	290	0.264	0.921	0.249	0.245
IV	290	0.275	0.872	0.281	0.280
V	290	0.185	1.813		
		0.261	0.891		
VI	290	0.265	0.852	0.253	0.254
	80	0.329	0.847	0.390	0.381
VII	290	0.201	0.995	0.274	0.386
	80	0.283	1.123	0.460	0.428

the method). This enables the observation in the spectrum of overlapping lines resulting from two different states. A similar effect was observed in mixed-valence complexes of [$Fe(II)Fe_2(III)O(CH_3COO)_6L_3$] type [13]. This constitutes additional evidence of the existence of a small but measurable delocalization in complexes of the trapped-valence electronic structure.

II. Compounds of Fe–pyz–Fe type

The compound with the Fe(II)–pyz–Fe(II) core is stable in solution and in the solid state. The products of one and two electron oxidation undergo co-proportionation [2] and the oxidized compounds cannot be obtained in pure form, either in solution or in solid state. In the spectrum of $[Fe(CN)_5pyz]^{3-}$ there is a bathochromatic shift of the d → π* band at 454 nm to 505 nm due to dimerization. On the other hand, the one electron oxidation results in a hypsochromatic shift of that band to 458 nm, whereas such a shift has not been observed in the diffuse reflectance spectrum of this compound. Furthermore, a band appears in the NIR region at about 1200 nm. The position of this band is independent of the bridging ligand [2] which suggests that this band also should be attributed to unidentified decomposition products of Fe(II)–pyz–Fe(III). This fact brings in question the estimation of the Husch's delocalization parameter [14] carried out for this compound by Felix and Ludi [2].

The Mössbauer spectrum of the one electron oxidation product consists of two doublets of different intensity (Table I, Fig. 2). The inner doublet has IS and QS parameters corresponding to those of the initial compound Fe(II)–pyz–Fe(II). The outside doublet parameters indicate its origin from the low-spin Fe(III) and are very close to those reported by Burger *et al.* [15] for $Na_2[Fe(III)(CN)_5L]$. The low intensity of the outside doublet in comparison with that of the initial compound constitutes evidence for the mentioned above co-proportionation and equilibrium shift towards the Fe(II)–pyz–Fe(II) system. Stability of IS values of Fe(II) moiety for Fe(II)–pyz–Fe(II) and Fe(II)–pyz–Fe(III) is related to lack of π-acceptivity properties of the $[Fe(III)(CN)_5]^{2-}$ unit.

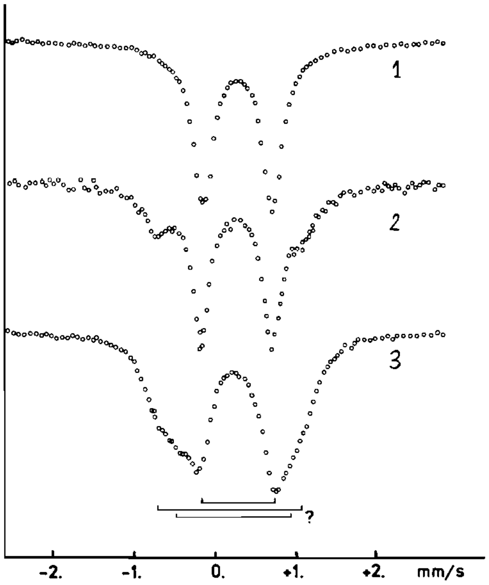

Fig. 2. Mössbauer spectra of the complex: $Na_6[(CN)_5Fe-pyz-Fe(CN)_5]\cdot 8H_2O$ (1) and its one- (2) and two-electron oxidation products (3).

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