Inorganica Chimica Acta, 34 (1979) L185–L186

Mössbauer Studies on Bis(4-substituted pyridine)iron-(II) Thiocyanate

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Received January 13, 1979

In previous works we have shown that some 3- or 4-substituted pyridine complexes of high-spin iron(II) display two quadrupole doublets of Mössbauer spectra at low temperature [1–3]. This preliminary evidence has never been interpreted. The present work has undertaken a more rigorous investigation of the temperature-dependent Mössbauer studies for the complexes of $FeL_2(NCS)_2$ (L = py, $4\text{-}CH_3\text{-}py$, 4-Cl-py, $4\text{-}CH_3CO\text{-}py$ and $4\text{-}C_6H_5\text{-}py$). The results suggest that two states of iron ions are present in the different configuration in the iron(II) complexes.

Experimental

The complexes $FeL_2(NCS)_2$, with the exception of $Fe(4\text{-}C_6H_5\text{-}py)_2(NCS)_2$ and $Fe(4\text{-}CH_3CO\text{-}py)_2(NCS)_2$, were prepared by the thermal decomposition of corresponding $FeL_4(NCS)_2$ under a nitrogen stream [1, 4]. $Fe(4\text{-}R\text{-}py)_4(NCS)_2$, (R = H, CH_3, Cl) were prepared by the method of Golding, *et al.* [5].

$Fe(4\text{-}C_6H_5\text{-}py)_2(NCS)_2$ and $Fe(4\text{-}CH_3CO\text{-}py)_2(NCS)_2$ were prepared as follows: $FeSO_4\cdot 7H_2O$ (0.016 mol) in 10 ml of water was added to $NH_4(NCS)$(0.032 mol) in 3 ml of water, then 0.032 mol of ligands in 10 ml of ethanol were added and the products were collected and washed with three 5 ml portions of ethanol–water solution, and dried *in vacuo*.

Anal. Calcd for $Fe(4\text{-}C_6H_5\text{-}py)_2(NCS)_2$: Fe, 11.4; C, 59.9; H, 3.74; N, 11.6. Found: Fe, 11.0; C, 59.4; H, 3.80; N, 11.5.

Calcd for $Fe(4\text{-}CH_3CO\text{-}py)_2(NCS)_2$: Fe, 13.5; C, 46.4; H, 3.38; N, 13.5. Found: Fe, 13.1; C, 47.0; H, 3.41; N, 13.2.

Calcd for $Fe(4\text{-}CH_3\text{-}py)_2(NCS)_2$: Fe, 15.6; C, 47.0; H, 3.91; N, 15.6. Found: Fe, 15.2; C, 47.2; H, 3.85; N, 15.2.

Calcd for $Fe(4\text{-}Cl\text{-}py)_2(NCS)_2$: Fe, 14.0; C, 36.1; H, 2.00; N, 14.0. Found: Fe, 13.9; C, 36.7; H, 1.82; N, 14.2.

Calcd for $Fe(py)_2(NCS)_2$: Fe, 14.7; C, 37.9; H, 2.63; N, 14.7. Found: Fe, 14.9; C, 37.4; H, 2.70; N, 14.8.

IR spectra of the complexes were taken at 298 K with a Beckman Model 4250(4000–200 cm^{-1}) grating spectrophotometer. Magnetic moments were measured by using a room temperature Gouy balance Newport MK.II.

Mössbauer spectra in the temperature range 78–298 K were measured with an ASA-600 Mössbauer spectrometer. The source $^{57}Co(Rh)$ was used and kept at room temperature. The isomer shifts were defined using sodium nitroprusside as standard.

Results and Discussion

The magnetic moments (μ_{eff}) and the most important IR absorption bands are given in Table I. All the values of μ_{eff} at room temperature for the complexes of iron(II) range from 5.04 to 5.60 B.M. and are consistent with the magnetic moments expected for distorted octahedral high-spin iron(II).

$Fe(py)_4(NCS)_2$ and $Fe(4\text{-}CH_3\text{-}py)_4(NCS)_2$ are known to have *trans*-octahedral configuration about the iron atom [6, 7], *i.e.* nitrogen atom of –NCS– is *trans* to iron atom. The crystal structures of Fe(4-

TABLE I. Magnetic moments and the Most Important IR Data (cm^{-1}) for the Complexes. [a]

Compound	μ_{eff}(B.M.) (298 K)	ν_{CN}	ν_{CS}	ν_{NCS}	ν_{Fe-NCS}
$Fe(py)_2(NCS)_2$	5.39	2090 (vs) 2050 (sh)	780	470 490	262
$Fe(4\text{-}CH_3\text{-}py)_2(NCS)_2$	5.29	2090 (vs) 2060 (sh)	783	470 482 490	269
$Fe(4\text{-}C_6H_5\text{-}py)_2(NCS)_2$	5.28	2093 (vs) 2060 (sh)	–	470 478	256
$Fe(4\text{-}CH_3CO\text{-}py)_2(NCS)_2$	5.04	2095 (vs) 2050 (sh)	784	472 485	265
$Fe(4\text{-}Cl\text{-}py)_2(NCS)_2$	5.10	2085 (vs) 2065 (sh)	780	468 490	260

[a] vs: very strong, sh: shoulder.

TABLE II. Mössbauer Data for the Complexes.

Compound	Isomer Shifts (mm/sec)[a]			Quadrupole Splittings (mm/sec)[b]		
	78 K	202 K	298 K	78 K	202 K	298 K
$Fe(py)_2(NCS)_2$	1.34	1.26	1.24	3.07	2.91	2.59
$Fe(4\text{-}CH_3\text{-}py)_2(NCS)_2$	1.34	1.28	1.26	3.16	3.06	2.72
	1.34	1.28	1.25	1.78	1.43	1.09
$Fe(4\text{-}Cl\text{-}py)_2(NCS)_2$	1.30	1.26	1.24	3.12	2.90	2.80
	1.31	1.27	1.25	1.85	1.62	1.41
$Fe(4\text{-}C_6H_5\text{-}py)_2(NCS)_2$	1.34	1.34	1.29	3.16	2.96	2.62
$Fe(4\text{-}CH_3CO\text{-}py)_2(NCS)_2$	1.51	1.41	1.36	1.93	1.83	1.73

[a] ±0.02 mm/sec. [b] ±0.03 mm/sec.

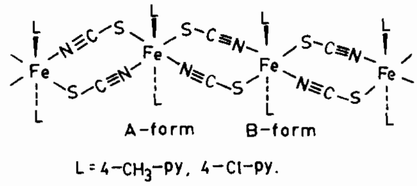
R-py)$_2$(NCS)$_2$ are not known. However, from X-ray, IR and Mössbauer studies [1], it seems that Fe(py)$_2$(NCS)$_2$ is isomorphous with Co(py)$_2$(NCS)$_2$, whose structure is known [8], hence Fe(py)$_2$(NCS)$_2$ seems an octahedral polymeric structure with bridging NCS ions.

The comparison of IR spectra (as shown in Table I) of Fe(4-R-py)$_2$(NCS)$_2$ also suggests the presence of bridging thiocyanate groups since for NCS bridging complexes, it covers a wide range of 2090–2200 cm^{-1} for CN stretching frequencies [9].

Mössbauer spectra

The Mössbauer parameters are collected in Table II. The isomer shifts for the complexes I.S. = 1.30–1.40 mm/sec are located in the range of expected values for high-spin iron(II) complexes with the electronic configuration $t_{2g}^4e_g^2$.

The Mössbauer spectra of Fe(4-CH$_3$-py)$_2$(NCS)$_2$ and Fe(4-Cl-py)$_2$(NCS)$_2$ clearly exhibit two doublets quadrupole splittings and same isomer shifts. This implies that two sites of iron atoms exist in the complexes; in addition, the ratio of abundance for the two site irons is near 1:1, and this ratio does not change with temperature. It may be seen from Table II that the quadrupole splittings for the outer doublet of the Fe(4-CH$_3$-py)$_2$(NCS)$_2$ and Fe(4-Cl-py)$_2$(NCS)$_2$ are near to those of structure known Fe(py)$_2$(NCS)$_2$, so that, one site of iron atom in these two complexes may be taken as *trans*-configuration of NCS (B-form), *i.e.* nitrogen atom of NCS is *trans* bonded to the iron atom. In the other site, the smaller quadrupole splitting of iron atom may be taken as *cis*-configuration (A-form), *i.e.* nitrogen atom of NCS is *cis*-bonded to the iron atom. The configuration could be suggested as shown in Fig. 1, and the real crystal structure must be determined with single crystal X-ray study. A detailed discussion will be presented in a future report.



L = 4-CH$_3$-py, 4-Cl-py.

The larger difference in quadrupole splitting values between A-form and B-form configurations may be attributed to the different asymmetric population of the sixth electron of 3d^6 among the t_{2g} orbitals, with the energy separations of $\delta_{t_{2g}}$ between the $b_{2g}(d_{xy})$ and $e_g(d_{xz}, d_{yz})$. From theoretical treatments of Ingall [10] and Gibbs [11], the crystal-field splitting $\delta_{t_{2g}}$ could be estimated. In addition, a larger quadrupole splitting (above 2 mm/sec) is generally expected for a tetragonal distortion with d_{xy} lowest, while for d_{xz} and d_{yz} lowest the quadrupole splitting is about half the magnitude. On the basis of this model, the S.Q. values of Fe(L)$_2$(NCS)$_2$ (L = py, 4-CH$_3$, 4-Cl, 4-C$_6$H$_5$) are much larger and suggest that in each case the orbital ground state is possibly d_{xy}. The obtained values of $\delta_{t_{2g}}$ for Fe(py)$_2$(NCS)$_2$, Fe(4-C$_6$H$_5$-py)$_2$(NCS)$_2$, B-form Fe(4-Cl-py)$_2$(NCS)$_2$ and B-form Fe(4-CH$_3$-py)$_2$(NCS)$_2$ are 460, 320, 450 and 480 cm^{-1} respectively in the case of d_{xy} lowest and for Fe(4-CH$_3$CO-py)$_2$(NCS)$_2$, A-form Fe(4-Cl-py)$_2$(NCS)$_2$ and A-form Fe(4-CH$_3$-py)$_2$(NCS)$_2$ are 430, 310 and 200 cm^{-1} respectively in the case of d_{xz}, d_{yz} lowest.

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