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Spectroscopic Properties and Bonding Character of Thiocyanate Ligand in Some Pyridine and 2,2'-Dipyridyl Ru(II) Mixed Complexes

STANISLAW WAJDA, KRYSTYNA RACHLEWICZ

Institute of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383 Wroclaw, Poland

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A method of obtaining mixed pyridine and 2,2'-dipyridyl thiocyanate complexes has been worked out. Examination of IR spectra in the mean and far infrared region as well as studies of electronic and CD spectra allows to determine the complexes obtained as cis-*[Ru(py)$_4$(NCS)$_2$] and* cis-*[Ru(bipy)$_2$(NCS)$_2$]. On the basis of the examinations and integrated intensity values of ν_{C-N} bands the occurrence of N-bonded thiocyanate ligand in the complexes has been established. Linkage isomery, however, has not been observed.*

The formation of N bonding in the complexes in the presence of soft donors (bases) determines the nature of Ru(II) ion as acceptor with class b *(soft) Lewis acid properties in terms of HSAB principle.*

Introduction

There have been an increasing number of reports on the chemistry of ruthenium, while reports on Ru(II) thiocyanate complexes have been comparatively few. Substitution reaction of thiocyanate groups in optically active Ru(II) complexes of type $[Ru(phen)_2(py)_2]^{2+}$, $[Ru(H_2O)(bipy)(terpy)]^{2+}$, $[Ru(bipy)_2(H_2O)_2]^{+2}$ [1] and $[Ru(bipy)(terpy)Cl]^{+}$ [2] has been obtained. However, there is a lack of information about the bonding character of thiocyanate groups in these complexes.

The mode of bonding of the thiocyanate ligand is often used as a test of hard or soft metal properties [3]. The mode of bonding of the thiocyanate ligand depends not only on the nature of metal in terms of HSAB principle but on the nature of neutral ligands [4] in mixed ligand thiocyanate complexes as well.

Using Klopman's development [5], Norbury [6] has calculated softness parameters for the thiocyanate ligand, taking into account the two highest occupied orbitals with σ-symmetry, σ_3 and σ_4. Norbury has demonstrated that the hardest center available is the nitrogen atom of σ_4 so that this is the most likely donor to the hardest Lewis acid, namely, a class *a* metal surrounded by hard ligands. The softest center is also a nitrogen atom but this time of σ_3, and it will bond to the softest Lewis acid available which this time would be a class *b* metal surrounded by soft ligands. Intermediate situations involving class *a* metals with soft ligands or class *b* metals with hard ligands would each prefer to coordinate with the sulfur atom. Thus it justifies Jϕrgensen's [7] idea of symbiosis as well as finds confirmation in most of experimental data. The influence of other factors (steric effect) may account for a few exceptions.

The object of the paper presented here has been to determine the mode of bonding of the thiocyanate ligand in mixed ligand Ru(II) complexes with pyridine and 2,2'dipyridyl (soft bases) thereby determining the nature of Ru(II) ion in terms of HSAB principle.

Experimental

The Preparation of Complexes

[Ru(py)$_4$(NCS)$_2$]

1 g of $RuCl_3x3H_2O$ was dissolved in 500 ml of ethanol and 3 g of NaSCN and 30 ml of pyridine were added. The mixture was refluxed for 3 days upon which the solution was kept in a dark bottle for one week after which time the unidentified brown precipitate was filtered. From the evaporated solution the yellow-green precipitate came down which was a mixture of Ru(II) and Ru(III) complexes. The components were then isolated on a chromatographic column filled with the "Merck" magnesium silicate. The complex under study was eluted with chloroform. After evaporating excess chloroform in a rotary evaporator and adding about 2 ml of pyridine the crystals of the complex, which contained solvated pyridine, were precipitated. Upon washing with ethanol and drying, the complex underwent desolvation with a simultaneous destruction of crystal lattice. In its solid state the complex is stable and insensitive to oxidation.

A derivatographic analysis showed that the complex was not solvated. The complex obtained is diamagnetic.

Results of the analysis

Calculated:	% Ru	% C	% H	% N	% S
	19.0	49.5	3.7	15.7	11.99
Found:	18.9	49.6	3.6	15.85	11.7

The complex in DMF solution is a non-electrolyte (R = 267000 Ω)

[Ru(2,2'bipy)₂(NCS)₂]

1 g of $RuCl_3 x 3H_2O$ was dissolved in 250 ml of ethanol upon which 1.2 g of 2,2'dipyridyl in 150 ml of alcohol were added. Upon mixing the solutions a brown precipitate came down. The solution with the slurry was refluxed for 2 days at alcohol boiling temperature. After filtering the residue, 1.8 g of NaSCN were added to the filtrate and the solution was kept boiling for 24 h during which time dark brown–violet crystals precipitated. After filtering they were washed with water several times and then with alcohol.

The complex is diamagnetic and in DMF solution is a non-electrolyte (R = 220000 Ω).

Results of the analysis

	% Ru	% C	% H	% N	% S
Calculated:	19.2	49.9	3.0	15.08	12.0
Found:	19.17	49.5	3.0	15.27	11.8

Analysis

The amount of C, H, N and S was determined by elementary analysis while ruthenium was determined by the modified method of Ayres and Young [8].

Measurements

Absorption spectra in acetonitrile, DMF and chloroform solutions and the reflection spectrum in Li_2CO_3 pellet were recorded on a Cary-14 and Hitachi Spectrophotometer.

CD spectra in DMF solutions were recorded on a spectropolarymeter Model ORD/UV-5 Japan Spectroscopic Co. LTD, Tokyo.

IR spectra at 4000–400 cm^{-1} were recorded in KBr pellet and nujol. IR spectra in DMF solution at 2050–2150 cm^{-1} and the spectra in nujol in the far infrared region were recorded on a Perkin-Elmer PE 180 Spectrophotometer.

Integrated intensity "A" of ν_{C-N} band was calculated by the method of Ramsay [9] from the expression

$$A = \frac{\pi}{2cl} \ln \frac{T_o}{T} \Delta_{1/2} \ [M^{-1} \ cm^{-2}]$$

where : c, concentration (*M*); l, cell thickness; T_o, transmittance of solvent; T, transmittance of sample, $\Delta_{1/2}$, band width at half absorption maximum.

Molar conductance was measured in DMF (C = 10^{-3} *M*) solution on a Thompson-Wheatston bridge type MWT-77.

Magnetic measurements were performed by the method of Gouy.

Results and Discussion

IR Spectra

The IR spectrum of the complexes under study is typical of the presence of coordinated ligands pyridine and 2,2'dipyridyl [10–13]. All the bands of free ligands were reproduced with slight shifts and intensity changes. Substantial shifts of bands assigned to deformation vibrations of pyridine ring are characteristic of the coordinated ligands. Strong bands at 605 and 404 cm^{-1}, 399 and 619 cm^{-1} in the spectrum of the free pyridine and dipyridyl are observed in the spectra of their complexes as weak or mean intensity split bands at 640, 628, 482 and 460 sh (pyridyne complex) and 662, 655, 460 and 420, 414 (dipyridyl complex). Weak bands are observed in the spectra of the two complexes. These were not found in the spectra of free ligands. They are characteristic of coordinated ligands (1230 cm^{-1} in the spectrum of the complex with pyridine and 1309 cm^{-1} in the spectrum of the 2,2'dipyridyl complex). The splitting of the bands in the 400–1200 cm^{-1} region is also observed. The splitting of the bands in pyridine complex spectra has been studied by Clark and Williams [11]. They have found that splitting is observed only in monomeric hexacoordinated complexes containing 4 molecules of pyridine and it is independent of *cis* or *trans* configuration. Rao [14] has suggested that it may be connected with the interaction between pyridine molecules in crystal lattice of low symmetry or else it results from a slight rotation of the coordinated pyridine about the metal–nitrogen bond being however independent of metal environment symmetry.

The fact that no splitting is observed in the spectrum of $[Ru(py)_3(OH)(NCS)_2]$ complex [15] confirms the results of studies made by these authors.

Bands corresponding to thiocyanate fundamental frequencies [16] can be easily identified. The bands could be identified by comparing the positions of bands and their intensity in the spectra of the complexes with those observed in the spectra of the free ligands and mixed ligand chloride complexes. The results are summarized in Table I.

It can be seen from the data in Table I that the band positions are characteristic of coordination through nitrogen [16]. The high frequency of ν_{C-N} is connected with the presence of π acceptor ligands in the case of which the withdrawing of electron density from the filled metal orbitals into the empty antibonding orbitals of the organic ligand is observed.

Taking into account the spectra of the complexes under study recorded in DMF solution at 2050–2150 cm^{-1} (Fig. 1) we have found that the C–N bands are

TABLE I. Positions of Bands Corresponding to Thiocyanate Fundamental Frequencies.

Compound	ν_{C-N} (cm^{-1})	ν_{C-S} (cm^{-1})	δ_{NCS} (cm^{-1})
$Ru(py)_4(NCS)_2$	2092 (vs)	800 (vs)	484 (s)
$Ru(bipy)_2(NCS)_2$	2095 (vs)	800 (sh) 795 (vs)	482 (s)

TABLE II. Parameters of ν_{C-N} and the Values of Their Integral Intensity for the Complexes Studied.

Compound	ν_{max} (cm^{-1})	$\Delta_{1/2}$ (cm^{-1})	A/SCN × 10^{-4} (M^{-1} cm^{-2})
$Ru(py)_4(NCS)_2$	2089	18.2	8.2
$Ru(bipy)_2(NCS)_2$	2125	23.0	10.1

TABLE III. Far IR Spectra of Complexes Studied.

$Ru(py)_4(NCS)_2$	365 (vw) 310^b (w) 300^b (s) 268^a (s) 253^a (s) 270 (sh) 204 (s)
$Ru(bipy)_2(NCS)_2$	376 (vw) 367 (vw) 347^a (m) 328^a (w) 235^b (m) 221^b (m) 196^b (w)

$^a\nu_{Ru-NCS}$. $^b\nu_{Ru-N(py)}$ or $\nu_{Ru-N(bipy)}$.

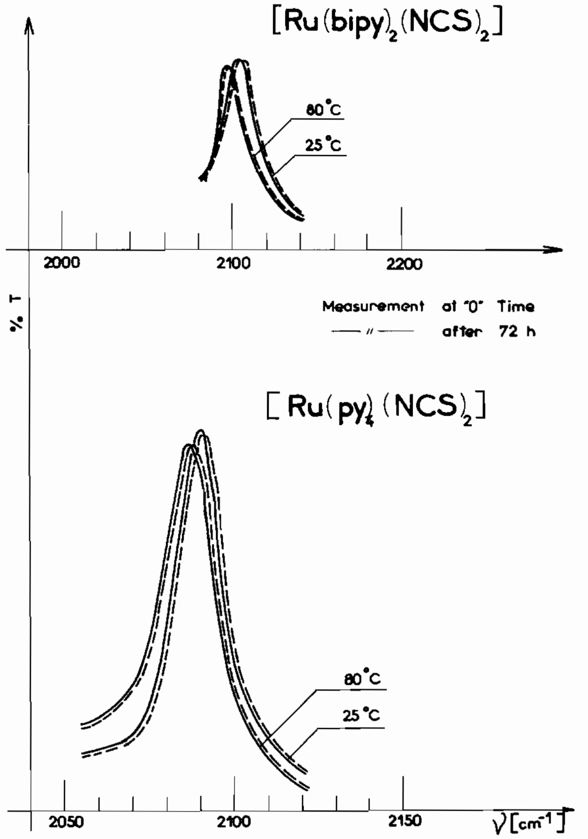

Figure 1. The dependence of the position and intensity of C–N bands on temperature and time of measurement. —— measurement at "0" time; - - - measurement after 72 h.

not split and the high integrated intensity values of these bands are characteristic of coordination through nitrogen [17]. The results are summarized in Table II.

The examinations of the dependence of positions and ν_{C-N} band integrated intensity on temperature (80 °C) and time (5 days) have shown that the process of linkage isomerization does not occur in the complexes under study [4].

A number of bands are observed in the far infrared region. Very weak bands at 365 cm^{-1} in the spectrum of pyridine complex and 376 and 367 cm^{-1} in the spectra of dipyridyl complex can be assigned to the vibrations of pyridine conjugated rings. In the case of pyridine they appear active only in the Raman spectrum. The bands can be activated as a result of coordination.

An intense band at 300 cm^{-1} and a weak one at 310 cm^{-1} can be assigned to valence vibrations of M–N (pyridine). The bands in this region were observed [11] in the spectra of a series of complexes $[Ru(py)_4X_2]$ (X = Cl, Br, I) independent of *cis* or *trans* symmetry of the complexes under study. Their high frequency, which was not to be found in the spectra of the complexes of other metals, should especially be noted. An increase of valence band frequency is expected in the complexes of metals with a low spin configuration d^6 as a result of a considerable stabilization of the ligand field. In spite of that, the bands at 287–240 cm^{-1} were assigned to these vibrations in the complexes of Ir(III) and Rh(III) [11].

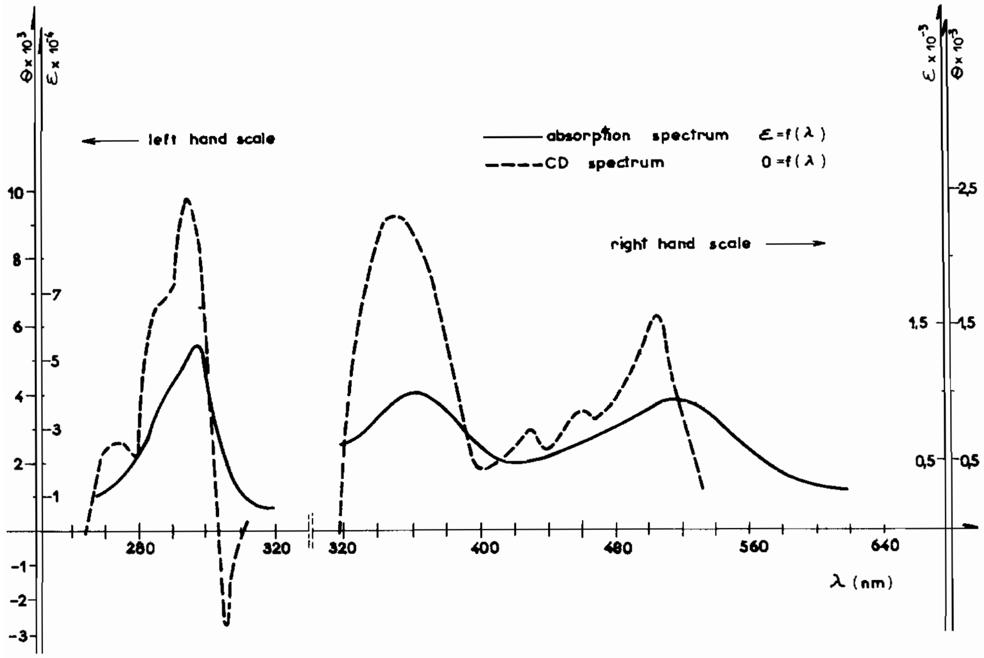

Figure 2. Absorption and CD spectra of $[Ru(bipy)_2(NCS)_2]$.

The splitting of the band at 268 and 253 cm^{-1} must be assigned to valence vibrations of Ru–thiocyanate ligand. In accordance with Forster's and Goodgame's [18] criterion the position of this band is indicative of the presence of coordination through sulfur in this complex. In the spectra of chloride and bromide complexes of the same symmetry (C_{2v}), the frequencies corresponding to valence vibrations at ν_{Ru-Cl} – 325 and 313 – and ν_{Ru-Br} – 175 and 168 cm^{-1} – were found [19].

The ν_{Ru-NCS} bands in the complex are characterized by high intensity typical of coordination through nitrogen. It is possible that the high stabilization of Ru–N(py) bonding causes a destabilization of Ru–NCS bonding, this being reflected in the decrease of frequency of the respective valence vibration.

In 2,2'dipyridyl complex spectrum the bands at 235, 221, 196 cm^{-1} can be assigned to $\nu_{Ru-N(bipy)}$ [20] vibrations whereas the bands at 347 and 328 cm^{-1} can be assigned to ν_{Ru-NCS} vibrations for the thiocyanate group coordinated through nitrogen. Since there is a lack of data on chloride complexes of Ru(II) a comparison of the position of these bands to ν_{Ru-Cl} (344, 321 cm^{-1}) bands observed in the spectrum of $[Ru^{III}(bipy)_2Cl_2]ClO_4$ [21] complex was used to determine the character of bonding in these complexes.

The numbers of stretching frequencies Ru–N (ligand) and Ru–NCS observed in the far IR spectra of the two complexes agree well with the expectations for *cis* configuration [22].

The position of ν_{C-N}, ν_{C-S}, stretching and δ_{NCS} bending frequencies as well as the position and intensity of Ru–NCS stretching frequencies and the integrated intensity values of ν_{C-N} bands are all indicative of N-bonding in the complexes studied.

Electronic and Circular Dichroism Spectra

CD and electronic spectra of $[Ru(bipy)_2(NCS)_2]$ are shown in Figure 2. The bands observed, extinction and molar ellipticity coefficients for both complexes under study have been summarized in Table IV.

The electronic spectra of both compounds are characteristic of metal complexes with a low spin d^6 configuration.

A shoulder observed at ~16000 cm^{-1} in the spectrum of the complex $[Ru(bipy)_2(NCS)_2]$ can be assigned to the spin forbidden d–d transition in spite of the high coefficient of extinction. The latter may be due to the borrowing of intensity from the adjacent highly intense CT band.

Charge-transfer transitions $d \rightarrow \pi^*$ from the filled orbitals of (t_2) metal into the vacant low lying antibonding π orbitals of dipyridyl (ϕ_7 and ϕ_8 – according to the MO dipyridyl [23] calculations) lie at 19720 and 27000 cm^{-1}.

In CD spectrum two bands are observed at 19760 and 23260 cm^{-1}. These can be assigned to the first spin allowed d–d transition $^1A_{1g} \rightarrow {}^1T_{1g}$ ($^1A_1$ + ^1E). The occurrence of the bands of this type in the complexes $[Ru(bipy)_2X_2]$ (where X = CN, 1/2 en, 1/2 phen, py, Cl, 1/2 ox) in the region in question has been suggested by Crosby *et al.* [24] as well as by Bosnich [25]. Splitting results from the low symmetry of the metal environment.

TABLE IV. Band Positions in Electronic Spectra of Ru(II) Complexes under Study.[a]

Type of spectrum Solvent Compound	Absorption				Reflection pellet	CD		Type of transition
	Acetonitrile		DMF		Li_2CO_3	DMF		
	Band position ($cm^{-1} \times 10^{-3}$)	$\epsilon \times 10^{-3}$	Band position ($cm^{-1} \times 10^{-3}$)	$\epsilon \times 10^{-3}$	Band position ($cm^{-1} \times 10^{-3}$)	Band position ($cm^{-1} \times 10^{-3}$)	$\theta \times 10^{-3}$	
1	2	3	4	5	6	7	8	9
$Ru(bipy)_2(NCS)_2$	16.7[a]	(1.5)	–	–	16.1[a]	–	–	d → d s.f.
	19.7	6.55	19.7	9.35	19.3	19.76	+1.6	d → $\pi^*(\phi_7)$ CT
	21.7[a]	(5.29)	21.7[a]	(6.0)	21.7[a]	21.74	+0.85	$^1A_{1g} \rightarrow {}^1T_{1g}$ ($^1A_1$ + ^1E)
						23.26	+0.70	
	27.7	6.85	27.5	9.81	27.0	28.57	+2.28	d → $\pi^*(\phi_8)$ CT
	33.9	45.8	33.5	59.9	33.5	32.66	−2.85	$\pi \rightarrow \pi^*$
	34.6[a]	35.3	34.5[a]	42.5	–	33.89	+9.70	
						35.0[a]	(+6.7)	d → π^* (ϕ_9) CT
						36.6	+2.6	$^1A_{1g} \rightarrow {}^1T_2$ d → d
	39.2[a]	?	–	–	–	–	–	$\pi \rightarrow \pi^*$ + CT and
	40.8	22.3	–	–	40.6	–	–	$2\pi \rightarrow 3\pi$ (SCN^-)
					46.7			
	Chloroform		DMF		pellet Li_2CO_3	DMF		
$Ru(py)_4(NCS)_2$	24.4[a]	(6.2)	23.8[a]	?	23.2	–	–	d → π^* (py)
	26.6	22.3	26.6	21.0	25.6	26.6	+4.8	+ d → d
	27.7[a]	(16.3)	27.7[a]	(15.7)	27.0	28.57[a]	(+2.8)	
						29.41[a]	(+1.6)	
					40.0			$\pi \rightarrow \pi^*$ (py)
					45.5[a]			$2\pi \rightarrow 3\pi$ (NCS^-)

[a] Shoulder.

Several bands are observed in absorption and CD spectra in the 32000–37000 cm^{-1} region (Table IV).

Two of them at 33890 and 32600 cm^{-1} with opposite circular dichroism effects, negative for the band with lower frequency, positive for the one with higher frequency, should be assigned to internal ligand $\pi \rightarrow \pi^*$ transition. According to Bosnich's [25] studies effects of this kind are typical of a complex with absolute *cis*(–)[M(dipy)$_2$X$_2$] configuration.

The assignment of the shoulder at 35000 cm^{-1} is difficult to make. Most probably it corresponds to a successive CT transition of the type d $\rightarrow \pi^*$ (ϕ_9). The corresponding band in [Ru(dipy)$_3$](SCN)$_2$x3-H$_2$O [15] complex was observed at 39210 cm^{-1}. It should be noted, however, that the shift of all CT bands toward higher frequencies was found in the spectrum of trisdipyridyl complex [26].

By contrast, this band was not observed in the Ru(III) complex [Ru(bipy)$_2$Cl$_2$]$^+$ [21] which gives strong support to such an assignment.

The band observed in CD spectrum at 36600 cm^{-1} is also difficult to interpret. The occurrence of the allowed CT transition from the filled π orbital of dipyridyl into the empty metal orbital (e) in this region is of little probability especially since the band has too low an intensity. By contrast, we can expect a successive spin allowed d–d ($^1A_{1g} \rightarrow {}^1T_{2g}$ in terms of O$_h$ symmetry) transition in this region.

At 40000–50000 cm^{-1} successive bands $\pi \rightarrow \pi^*$, d $\rightarrow \pi^*$ (ϕ_{10}) and $2\pi \rightarrow 3\pi$ (SCN) band are found. A detailed assignment, however, is not possible.

The spectrum of the pyridine complex has fewer bands. In absorption and CD spectrum only one intense band at 26600 cm^{-1} with a positive circular dichroism effect and two shoulders are observed. The intense band should be assigned to the charge-transfer transition of type d $\rightarrow \pi^*$(py) [27].

The presence of the first spin allowed d–d bands to which the shoulders observed can be assigned is expected in this region.

The band corresponding to the internal ligand transition $\pi \rightarrow \pi^*$ of pyridine and probably $2\pi \rightarrow 3\pi$ transition of thiocyanate group are to be observed at 40000–50000 cm^{-1}.

As can be seen from the data on charge transfer band position of type d $\rightarrow \pi^*$, 2,2'dipyridyl is a ligand characterized by decidedly stronger π acceptor properties, which is responsible for a greater shift of ν_{C-N} towards higher frequencies.

The difference in π acceptor properties of the two ligands under study does not affect the mode of bonding of the thiocyanate ligand. According to Norbury [4, 6] the occurrence of N-bonded thiocyanate ligand in the mixed-ligand complexes with π acceptor (soft) bases allows to establish Ru(II) ion as acceptor with class *b* (soft) Lewis acid properties.

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