Inorganica Chimica Acta, 31 (1978) 25–30
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Spectroscopic Properties and Mode of Bonding of Thiocyanate Ligand in Some Ru(III) Complexes

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Received December 30, 1978

The existence of a mixed mode of bonding of the thiocyanate groups by sulfur and by nitrogen in hexathiocyanato and tetrathiocyanato bisammine Ru(III) complexes has been confirmed recently. This conception has been accepted on the basis of both the analyses of vibrational spectra and a study of isotopic exchange kinetics and Mössbauer spectrum. The suggestions pertaining to the structure of complexes under study which have been discussed above find their confirmation in the results of studies of far infrared spectra, in the integrated intensity value of the ν_{C-N} band as well as in an analysis of electronic and circular dichroism spectra.

Introduction

Studies of the mode of bonding of thiocyanate groups in hexathiocyanato and tetrathiocyanato bisammine complex of Ru(III) carried out recently have pointed to the existence of these groups coordinated through both nitrogen and sulfur [1, 2].

Schwerdtfeger's and Preetz's [3] studies have confirmed the existence of the mixed mode of bonding in a hexathiocyanato complex. The suggestions have been based on an analysis of Raman and infrared spectra as well as on a considerable axial deformation of symmetry in the hexathiocyanato complex, which has been found to exist by various authors working independently. It has been observed in both solution and solid state. The former has been found through studies of isotopic exchange kinetics [4], as well as through polarographic studies [5], whereas the latter has been observed on the basis of a considerable quadrupole splitting found in the Mössbauer spectrum [1].

Thus a structure of hexathiocyanate Ru(III) complex has been put forward having a symmetry of the closest central ion environment D_{4h} with two groups in axial positions coordinated through sulfur and four groups coordinated through nitrogen in the equatorial plane.

In the case of the tetrathiocyanato bisammine complex a C_{2v} symmetry has been suggested where two molecules of ammonia are in *trans* position to two thiocyanate groups coordinated through nitrogen in the equatorial plane while the remaining two groups coordinated through sulfur are in axial positions.

The suggestions pertaining to the structure of complexes under study, which have been discussed above, find their confirmation in the results of studies of far infrared spectra, in the integrated intensity value of the ν_{C-N} band as well as in an analysis of electronic and circular dichroism spectra.

Experimental

The hexathiocyanate $[(C_4H_9)_4N]_3[Ru(CNS)_6]$ and tetrathiocyanato bisammine $[(C_4H_9)_4N][Ru(CNS)_4(NH_3)_2]$ complexes have been obtained by the method described in earlier papers [4].

Far IR spectra (fivefold dilution) in the nujol suspension have been recorded on a Perkin-Elmer PE-180 spectrophotometer. The spectra of the solutions (range 2000–2150 cm^{-1}) have been recorded on a PE-180 spectrophotometer.

The integrated intensity, A, of the bands resolved numerically [6] has been calculated by the method of Ramsay [7] from the equation

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

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

Absorption and reflection electronic spectra have been recorded on a Cary-14 and Hitachi spectrophotometer.

CD spectra have been recorded on a spectropolarimeter Model ORD/UV-5 Japan Spectroscopic Co. Ltd, Tokyo.

Results and Discussion

Among the well known criteria used to estimate the mode of bonding of the thiocyanate group the criterion of the intensity of ν_{C-N} band is considered particularly satisfactory [8].

The band in the hexathiocyanato and tetrathiocyanato bisammine is split. Lorentzian analysis has revealed the presence of two bands. The positions of the two bands split in solution reveal the existence of coordination through both nitrogen and sulfur. The splitting of bands in the solution may be due to the ligand dissociation, the process of linkage isomerization or some other activity of solvent as well as to a low symmetry of metal environment. The band shifting towards higher frequencies suggests that splitting does not result from the ligand being dissociated, as the appropriate band for the free ligand is to be observed at about 2050 cm^{-1}.

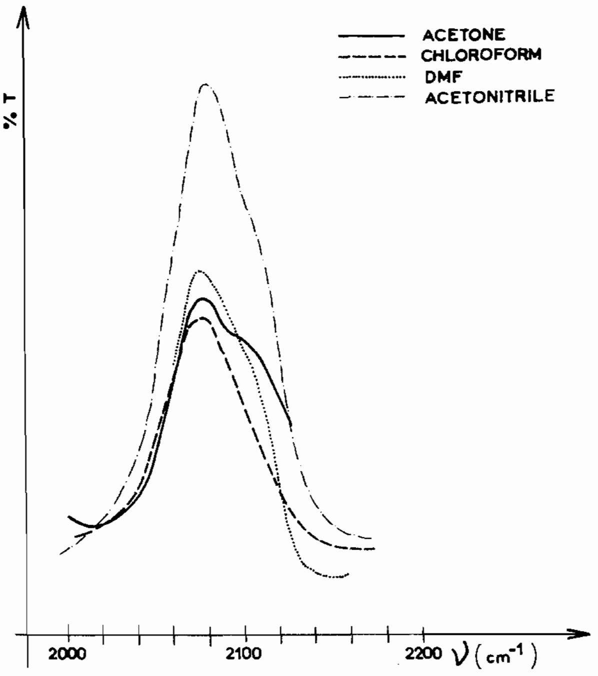

Figure 1. IR spectra at 2000–2150 cm^{-1} of $[Ru(SCN)_2(NCS)_2(NH_3)_2]^-$ in various solvents.

The positions of split bands in the case of $[Ru(CNS)_4(NH_3)_2]^-$ complex are independent of both the solvent (Fig. 1) and the measurement time beginning with the moment of the compound dissolution. The fact suggests a stability of forms responsible for the splitting of this band. Thus it cannot be connected with the process of linkage isomerization as the latter is characterized by a definite, easy-to-observe rate which depends on the nature of the solvent and time [9, 10, 11].

The conclusion is confirmed by a chromatographic analysis which has shown the homogeneity of solutions studied after a long period of time (5 days; the integrated intensity values have been calculated for the bands numerically resolved.

The value calculated for both bands indicates coordination through nitrogen (Table I). On the basis of the value calculated in this manner Bailey *et al.* [12] assumed the existence of coordination through nitrogen in hexathiocyanate complex of Ru(III).

The contribution of two thiocyanate groups to the intensity of two bands being assumed (per one thiocyanate group), the integrated intensity calculated for each band separately (Table I) indicates a coordination through nitrogen and sulfur. The contribution has been assumed mainly on the basis of the studies of isotopic exchange kinetics [4] and on the appearance of optical activity.

TABLE I. Data for Integrated Intensity and ν_{C-N} Band Positions for $[B_4N][Ru(CNS)_4(NH_3)_2]$ (A for M–NCS > 8 × 10^4 and for M–SCN < 3 × 10^4).

$\nu_{max}[cm^{-1}]$		$\Delta_{1/2}$ $[cm^{-1}]$	A/SCN × 10^{-4} $[M^{-1}\ cm^{-2}]$ calculated for	
Nujol mull	DMF solution		each bond separately	both
2098	2080	44.15	15.9	8.8
	2108	19.60	1.7	

Another criterion put forward by Forster and Goodgame [13] concerns the position of bands corresponding to valence vibrations ν_{M-CNS}. For complexes with the same composition and symmetry the following dependence is expected:

$$\nu_{M-NCS} > \nu_{M-Cl};\ \nu_{M-Br} < \nu_{M-SCN} < \nu_{M-Cl}$$

The bands observed in the spectra of complexes studied and the available data for hexachloride and hexabromide complexes of Ru(III) as well as Fe(III) in which the coordination through nitrogen in hexathiocyanate groups has been found are all listed in Table II.

In the spectrum of the complexes in question an additional band at 298 cm^{-1} is to be observed. It is,

TABLE II. Far IR data for Ru(III) and Fe(III) Complexes of $[MX_6]^{-3}$ Type.

Compound	ν_{M-X} Frequency, cm^{-1}		
	ν_{M-Cl}	ν_{M-CNS}	ν_{M-Br}
$[Ru^{III}X_6]^{-3}$	313[a]	335[b] 312[b]	242[a]
$[B_4N][Ru(CNS)_4(NH_3)_2]$	–	346[b] 312[b]	–
$[Fe^{III}X_6]^{-3}$	248[c]	270[d]	–

[a] D. G. Foyt, T. W. Siddall, H. C. J. Alexander, M. L. Good, *Inorg. Chem., 13,* 1793 (1974). [b] This work. [c] D. M. Adams, D. M. Morris, *J. Chem. Soc. (A)*, 694 (1968). [d] R. J. H. Clark, A. D. J. Goodwin, *Spectrochim. Acta, 26 (A),* 1254 (1968).

however, the band of tetrabutylammonium cation, as the same band is also to be found in the spectrum of butylammonium bromide.

The splitting of ν_{Ru-NCS} band can be found in the spectra of the complexes under study and the positions of the split bands are indicative of the presence of nitrogen and sulfur bonding.

Electronic and CD Spectra

Three criteria of electronic spectroscopy have been suggested in order to estimate the mode of coordination of these groups. The first refers to the position of d–d bands. It has been based on the difference between the position of ligand coordinated through nitrogen and that coordinated through sulfur in spectrochemical series. Thus one can expect these bands in the region of lower frequencies if the ligand coordinated through sulfur is concerned than in the case of nitrogen.

The second criterion concerns the position of the first CT band (from the filled orbitals of ligand into the empty metal orbital). The difference results from the value of the optical electronegativity for the ligand coordinated through nitrogen and sulfur. In the case of hexathiocyanate complexes of Ru(III) calculations [14] indicate that, the ligand coordinated through nitrogen being involved, one should expect the appropriate band at 17000 cm^{-1} while at 26000 cm^{-1} one would find the band for the ligand coordinated through sulfur.

A possibility of applying the position of internal ligand ($2\pi \rightarrow 3\pi$) band for determining the mode of linkage has also been considered [15, 16].

An analysis of a large number of data [10] allows to state that the position of d–d bands is the most adequate to the mode of bonding whereas the expected dependence in the case of [$2\pi \rightarrow 3\pi$] band fails to be observed.

One encounters a number of difficulties while interpreting the electronic spectra of 4d^5 electronic metals.

The difficulties that arise are due to:

(i) large number of possible electronic states for this configuration according to Tanabe–Sugano diagram [17]

(ii) considerable mixture of states owing to the spin–orbital coupling and

(iii) presence of low lying CT bands which cover the bands corresponding to d–d transitions.

Consequently considerable divergences of opinion in the interpretations of electronic spectra are to be noted even when the best known complexes of Ru(III) are concerned [18–29].

The bands to be observed in absorption, reflection and CD spectra of the complexes studied are given in Table III.

The bands at 15000 cm^{-1} to be observed mainly in the CD spectrum can be assigned to one of the spin-forbidden d–d transitions. The intensive band at ~18000 cm^{-1} can be assigned to $\pi_{CNS} \rightarrow d_{Ru}$ transition ($t_{1u} \rightarrow t_{2g}$ in terms of O_h symmetry taking the order of molecular orbitals of the ligand after Mc Caffery *et al.* [18]). In CD spectrum (Fig. 2) of the complex $[Ru(CNS)_4(NH_3)_2]^-$ the complex nature of this band is to be observed.

As the width of this band in the spectrum of hexathiocyanate complex is similar one can expect the band to be of a complex nature also in this case. The splitting of CT ($t_{1u} \rightarrow t_{2g}$ in O_h symmetry) band may be due to various reasons. The appearance of optical activity is connected with the low symmetry of the metal C_{2v} environment. Due to the removal of degeneracy the splitting of all levels with "t" symmetry occurs in the field characterized by such a low symmetry. The splitting of levels may be caused by the spin–orbital coupling. Jϕrgensen's [20], Schmidtke's [30] and other authors' [31] studies have shown that the value of spin–orbital coupling constant is substantial in the case of the thiocyanate ligand and may be responsible for the complex structure of absorption bands.

The presence of coordination through both nitrogen and sulfur may be third cause.

The interpretation of bands at ~24000 cm^{-1} frequency in the spectrum of hexathiocyanate complex as well as ~22000 cm^{-1} and ~30000 cm^{-1} in bisamminetetrathiocyanate is disputable. According to the available data [18–19] on the spectra of Ru(III) complexes with ligands located near thiocyanate group coordinated through nitrogen and sulfur in a spectrochemical series one can expect the first d–d bands in the region of 20000–35000 cm^{-1} for both modes of bonding. The bands in question display a too high coefficient of extinction (~2000) for one to assign them to d–d bands.

In papers on the interpretation of electronic spectra of 4d and 5d electron metals one can frequently find the bands with high coefficient of extinction assigned to d–d bands. The increase of band intensity is accounted for by a considerable mixing of d–d electronic states with odd charge-transfer ones as well as due to the spin–orbital coupling and an increase of bond covalency [32].

The analyzed bands in the spectra of complexes under study should be assigned to CT bands owing to a high coefficient of extinction as well as the dependence of their position on the solvent.

In CD spectrum one can be observe weak Cotton effect in the range 22000 cm^{-1} which testifies to the overlapping of two electronic transitions in this range. This may be connected with the overlapping of the band corresponding to CT transition on the first allowed d–d band.

The coordination through nitrogen and sulfur of thiocyanate groups in the complexes studied being assumed, there arises the question whether one can

TABLE III. UV–Visible Spectra of Ruthenium(III) Complexes under Study (* Shoulder).

Type of spectrum	Absorption				Reflection	CD		Band assignments
Solvent	Acetone		Ethanol		Li_2CO_3 pellet	Acetone		
Compound	Peak max. [cm^{-1}] × 10^{-3}	$\epsilon \times 10^{-3}$	Peak max. [cm^{-1}] × 10^{-3}	$\epsilon \times 10^{-3}$	Peak max. [cm^{-1}] × 10^{-3}	Peak max. [cm^{-1}] × 10^{-3}	$\theta \times 10^{-3}$	
$[B_4N]_3[Ru(NCS)_4(SCN)_2]$	15.6*	?	15.40*	?	15.15			d–d (?) (s. forb.)
D_{4h}	18.2	13.0	18.11	7.2	17.98			$t_{1u} \rightarrow t_{2g}$ (CT)
	25.0	4.0	24.20	2.5	23.80			$t_{2u} \rightarrow t_{2g}$ (CT) and d–d
					29.70*			$t_{1g} \rightarrow e_g$ (CT) or
					35.70*			d–d
			44.60*	>40.0	43.50			$2\pi \rightarrow 3\pi$ (CNS^-)
$[B_4N][Ru(NCS)_2(SCN)_2(NH_3)_2]$	15.1*	?	15.20*	?	15.15*	15.20	+0.65	d–d (?) (s. forb.)
C_{2v}	18.1	20.9	18.20	12.6	17.42	16.60	+0.70	$t_1 \rightarrow t_2$ (CT)
						17.39	+0.50	
						18.18	+1.10	
						18.90	+1.40	
	22.8	3.45	22.20	2.3	21.74	21.10	+0.50	d–d and $t_2 \rightarrow t_2$ (CT)
						22.30	−0.40	
	30.0	4.58	29.40	2.4	27.70			$t_2 \rightarrow t_2$ (CT)
					37.30			d–d (?)
			45.40*	>60.0	43.85			$2\pi \rightarrow 3\pi$

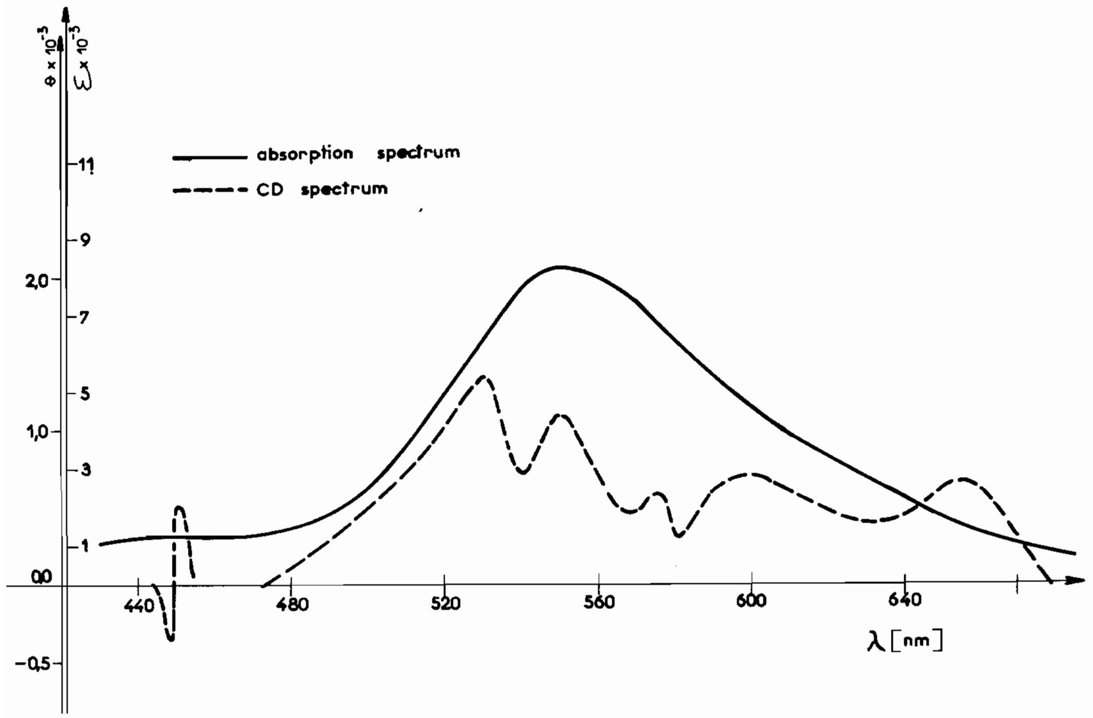

Figure 2. Visible absorption and CD spectra of $[Ru(SCN)_2(NCS)_2(NH_3)_2]^-$ in acetone solution.

observe separately the transitions from the orbitals of ligand coordinated through nitrogen and sulfur in the analyzed spectra of the range in question.

Thus it may be asked whether the bands observed in the ranges 20000–30000 cm^{-1} correspond to the next allowed CT transition from molecular orbitals of ligands ($t_{2u} \rightarrow t_{2g}$ in O_h symmetry) or whether they correspond to the first CT transition from the orbitals of the ligand coordinated through sulfur which is shown by the calculations [14]. The question of order of molecular levels in mixed complexes has been studied by many authors [32]. Mc Caffery *et al.* [18] studied absorption spectra as well as MCD of the complexes of low spin (d^5) metals of the type $[Ir^{IV}Cl_4X_2]^n$ where X = H_2O, NH_3, PPh_3, N_3^-, NCS^-. Absorption spectra and MCD of complexes of the type $(MX_5Y)^n$ where M = Fe(III), Ru(III); X = NH_3, CN^-, Y = H_2O, NH_3, PPh_3, N_3^-, NCS^-, have also been studied [24, 27, 33]. The studies have shown that no mixing of ligand orbitals is to be observed if the difference in the energy of filled orbitals of molecular ligands in mixed complexes and the higher symmetries of metal environment is considerable. The order of orbitals of essential ligand Cl, NH_3, CN is retained and their relative energies change only slightly.

In the spectrum one can observe the bands corresponding to independent transitions CT of the type $\pi_X \rightarrow t_{2(M)}$, $\pi_Y \rightarrow t_{2(M)}$. In the spectrum of Ru(III) complex one can find separate bands even in the case of ligands whose energies of the filled orbitals differ only slightly *e.g.* NH_3, Cl.

In lower symmetry fields one should expect a considerable mixing of orbital levels, which leads to a change of energy of all the filled ligand orbitals.

In the spectrum one can observe transitions of charge transfer type from the orbitals, which are a combination of orbitals of two ligands, even when ligands differing considerably in the level of energy *e.g.* Cl, PPh_3 are involved.

The conclusion, then, is that in the spectra of two complexes studied one should not expect separate bands for ligands coordinated through nitrogen and sulfur.

The analysed bands at 25000 cm^{-1} in the spectrum $[Ru(CNS)_6]^{3-}$ as well as at 22000 and 30000 cm^{-1} in the spectrum $[Ru(CNS)_4(NH_3)_2]^-$ can be interpreted as bands corresponding to successive transitions CT ($t_{2u} \rightarrow t_{2g}$ in terms of O_h symmetry) which cover the first d–d bands.

The effect of differentiated bonds may be reflected in both the position and the complex structure of the first CT band. The nature of weak shoulders (29700; 35000 cm^{-1}) for $[B_4N]_3[Ru(CNS)_6]$ and 27400, 37300 cm^{-1} for $[B_4N][Ru(CNS)_4(NH_3)_2]$ observed in the reflection spectrum is ambiguous, as in this range one can expect successive d–d bands as well as the first Laport-forbidden CT transitions which are activated in the field with low symmetry.

The intensive bands at 43000 cm^{-1} in the spectra of both complexes can be assigned to the transition inside the thiocyanate group ($2\pi \rightarrow 3\pi$).

An analysis of electronic spectra of thiocyanate complexes of Ru(III) under study shows that the first d–d bands covered with more intense bands CT are below the frequency observed in the spectra of Ru(III) complexes with ligands forming the mean field (*i.e.* ethylenediamine, ammonia) below the value expected for the coordination through nitrogen only.

Thus electronic spectra are not sufficient for determining the mode of linkage of thiocyanate groups in the complexes under study. However, the appearance of the first d–d bands at frequencies lower than the expected ones only for the coordination through nitrogen as well as the position and complex structure of CT band to be observed in the CD spectrum do not disagree with the conception of the coordination of thiocyanate groups through nitrogen and sulfur. This conception has been accepted on the basis of studies of vibrational spectra, Mössbauer spectrum and isotopic exchange kinetics.

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