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INFLUENCE OF THE PYRIDINE METHYL SUBSTITUENT POSITION ON THE CHEMICAL CHANGES OF THE NCS GROUPS IN THE THERMAL DECOMPOSITION OF COORDINATION COMPOUNDS OF THE TYPE $Cu(NCS)_2L_2$

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The influence of the position of the CH_3 group in picoline and lutidine ligands on the degree of chemical change of the NCS groups in coordination compounds of the type $Cu(NCS)_2L_2$ (where L = 2-, 3- and 4-picoline, and 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-lutidine) is dealt with. The most marked effect of the CH_3 group is found to be exerted in position 4. This effect of the methyl group on the degree of chemical change points to the mutual influence of the ligands in coordination compounds of Cu(II).

In a previous paper [1] we reported the thermal properties of thiocyanatocopper(II) complexes with all isomeric forms of picolines and lutidines. From the series of compounds studied, only $Cu(NCS)_2(3,5\text{-lut})_2$ shows a rather similar course of thermal decomposition to that of the complex $Cu(NCS)_2(py)_2$. In these compounds the release of the heterocyclic base and the polymerization and decomposition reactions of the NCS groups take place in separate steps. The other complexes studied exhibit a very complicated thermal decomposition up to 300°. At higher temperatures, 300 – 600°, the DTG curves are linear and the TG curves show only a uniform loss of weight of the sample with temperature. The intermediates of thermal decomposition after the first step have non-stoichiometric composition. From the composition and some physico-chemical properties of these intermediates we may suggest the influence of the position of the methyl substituent in the ligand L on the degree of chemical changes of the NCS groups in the thermal decomposition of coordination compounds of the type $Cu(NCS)_2L_2$, (where L = 2-, 3- and 4-picoline, and 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-lutidine).

Experimental

Preparative and analytical methods

Thiocyanatocopper(II) complexes of composition $Cu(NCS)_2L_2$ were prepared according to [4]. The intermediates of the first step of thermal decomposition were obtained by thermal degradation (to $\approx$300°) of the initial compound in a nitrogen atmosphere until the respective weight was reached (according to the thermal curves) (Table 1).

The Cu contents of the intermediates were determined complexometrically [2], and the N and C contents by using organic analyses. The S contents were measured gravimetrically as $BaSO_4$, after oxidation with concentrated HNO_3 and HCl in a solution of KI [3]. The results are listed in Table 1.

Table 1

The substance released from the starting compound and the analytical composition of the intermediates

Compound $Cu(NCS)_2L_2$ L =	Loss of weight, %	Components, %				Atom ratio			
		Cu	S	N	C	Cu	S	N	C
3,5-lut	59	39.02	27.78	16.65	14.54	1.00	1.41	1.94	1.97
2,5-lut	64	44.24	23.68	13.49	14.86	1.00	1.16	1.38	1.78
3-pic	58	39.78	23.30	17.29	17.90	1.00	1.06	1.38	1.78
2-pic	61	42.35	20.10	16.86	18.34	1.00	0.94	1.81	2.29
2,6-lut	64	43.47	19.42	15.79	16.93	1.00	0.89	1.65	2.06
2,3-lut	61	40.10	16.20	14.77	20.35	1.00	0.80	1.67	2.69
2,4-lut	61	37.51	14.98	12.79	23.59	1.00	0.79	1.55	3.33
3,4-lut	64	38.77	14.65	16.20	27.08	1.00	0.75	1.90	3.69
4-pic	61	42.49	13.22	16.21	23.23	1.00	0.62	1.73	2.89

Apparatus

The thermal decomposition was studied with a derivatograph (MOM, Hungary) [5]. The crucible used was 14 mm in diameter and the thermocouple was Pt/Pt-Rh. The 100 mg sample was powdered (grain size below 0.06 mm). The heating rate was 9°/min, the temperature range being 20–600°; measurements were performed in a nitrogen atmosphere.

The X-ray powder diffractograms of the intermediates were taken with a GON III diffractograph (Chirana, Praha). CuK_α radiation and a Ni filter were used.

The infrared absorption spectra of the intermediates were measured in Nujol uspension, using KBr windows, in the range 2000–2400 cm^{-1}, with a UR-20 spectrophotometer (Zeiss, Jena).

Results

Analytical evaluation of the intermediates of the complexes under investigation (Table 1) showed that only that of $Cu(NCS)_2(3,5\text{-lut})_2$ may be expressed by the formula $Cu_2S_3(CN)_4$; this was analytically demonstrated as an intermediate from the thermal decomposition of α-$Cu(NCS)_2(py)_2$ in [6]. In all other cases the compounds were found to be of non-stoichiometric composition.

As Table 1 shows, the intermediates may be divided according to their sulphur content into three groups. The first group covers the intermediates from the compounds with 3-pic, 3,5- and 2,5-lut; the second from those with 2-pic and 2,6-lut; and the third from those with 4-pic, 3,4-, 2,4- and 2,3-lut. It was found that, though belonging to the same group, the intermediates exhibit different physico-chemical properties.

Powder-diffractograms of intermediates from thermal decomposition

The diffraction angles in the powder diffractograms of the thermal decomposition intermediates are listed in Table 2. It follows from this Table that the diffractograms of the first group of intermediates differ from the others by the missing diffraction of $2\theta = \approx 11-15°$ and 28° and by the diffractions presents at $2\theta = \approx 16°$, $\approx 35°$ and $\approx 50°$. Only for this group of intermediates were all the reflections belonging to CuNCS observed. The remaining intermediates may again be divided into two groups according to the diffractions with angles $2\theta = \approx 29.5°$, $\approx 38°$ and $\approx 48°$. The intermediates of $Cu(NCS)_2(2,3\text{-lut})_2$ appears to form a transition between the second and the third groups. An intermediate exhibiting diffractions at $2\theta = \approx 30°$ and $\approx 48°$ may be assigned to the second goup, but the missing diffraction at $2\theta = \approx 33°$ shifts it to the third one.

Table 2

The diffraction angles of X-ray powder diffractograms in the intermediates of thermal decomposition

	CuNCS	Intermediate of thermal decomposition of compounds $Cu(NCS)_2L_2$ for L =								
		3,5-lut	2,5-lut	3-pic	2-pic	2,6-lut	2,3-lut	2,4-lut	3,4-lut	4-pic
Diffraction angle 2θ, °	—	—	—	—	11—15	11—15	11—15	11—15	11—15	11—15
	16.1	16.3	16.1	16.2	—	—	—	—	—	—
	27.2	27.3	27.1	27.2	27.0	27.2	27.2	27.3	27.2	27.2
	—	—	—	—	27.8	27.9	27.9	27.9	27.7	27.7
		29.3	29.2	29.2	29.4	29.4	29.5	—	—	—
		31.8	31.7	32.0	31.9	31.9	32.3	32.4	32.2	32.1
	32.6	32.7	32.6	32.7	32.9	33.0	—	—	—	—
	34 6	34.7	34.8	34.8	—	—	—	—	— —	—
		—	46.1	46.2	46.3	46.3	46.3	46.3	46.1	46.0
	47.2	47.1	47.0	47.1	—	—	—	—	—	—
		48.0	48.0	47.9	48.0	48.0	48.0	—	—	—
	50.1	50.1	50.0	50.0	—	—	—	—	—	—

The infrared spectra of the thermal decomposition intermediates

The presence of the thiocyanate group in the intermediates was investigated by means of their infrared absorption spectra. It was found (see Fig. 1) that only

for the first group of thermal decomposition intermediates were two absorption bands observed, at 2180 and 2115 cm^{-1}. The intermediates of compounds with 2-pic and 2,6-lut showed only very weak bands, while for those of the third group no bands could be observed.

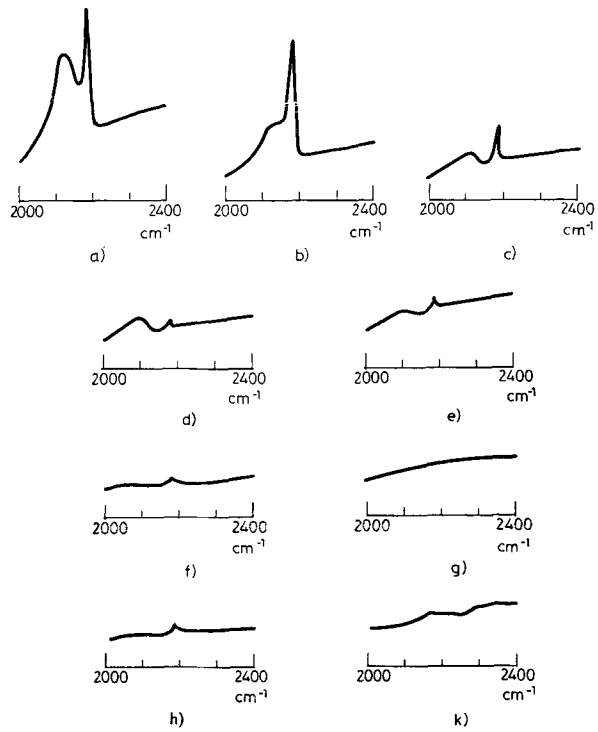

Fig. 1. Absorption bands of the valence vibration $\bar{\nu}$(CN) in intermediates of thermal decomposition of compounds $Cu(NCS)_2L_2$, L being a) 3,5-lut, b) 3-pic, c) 2,5-lut, d) 2,6-lut, e) 2-pic, f) 2,3-lut, g) 2,4-lut, h) 3,4-lut, k) 4-pic

The gradual extinction of the absorption bands in the shown order of the intermediates indicates, in agreement with the results of phase analysis of the powder diffractograms, that the greatest destruction of the thiocyanate group occurs in the last group.

Evidence of the presence of a polymeric NCS group in the thermal decomposition intermediates

Evidence of the presence of the polymeric NCS group was given by reaction of the thermal decomposition intermediates with concentrated HNO_3, according to [7]. In the case of a positive reaction sulphur is deposited from the solution

in the form of a yellow insoluble residue. The results obtained (Table 3) confirmed the conclusions from the foregoing measurements and showed that only the intermediates of the first group contain the polymeric thiocyanate group.

Discussion

From the physico-chemical properties of the thermal decomposition intermediates, the starting Cu(II) compounds may be divided into three groups:
1. compounds with 3-pic, 3,5- and 2,5-lut;
2. compounds with 2-pic and 2,6-lut;
3. compounds with 4-pic, 3,4- and 2,4-lut.

The intermediate of $Cu(NCS)_2(2,3\text{-lut})_2$ cannot be assigned unambiguously to the 2nd or the 3rd group. Its exceptional position is apparently due to the fact that this compound exhibits a different stereochemistry [4]. The presence of copper thiocyanate and the polymeric thiocyanate group was indicated only for the intermediates of the 1st group. For the intermediates of the other compounds the degree of decomposition of the thiocyanate group is higher.

The presence of picoline ligands in each of the three groups indicates not only that the methyl substituents influence the course of thermal decomposition, but also that their action is individual and depends on their position on the pyridine ring. The greatest decomposition of the thiocyanate groups, shown also by the lowest content of sulphur in the intermediate, occurs in $Cu(NCS)_2(4\text{-pic})_2$. The

Table 3

Results of reactions intermediates of thermal decomposition with concentrated HNO_3

Intermediate of $Cu(NCS)_2L_2$ for L =	Colour of the intermediate	Results of the reaction with concentrated HNO_3
3,5-lut	Cinnamon brown	Blue solution + yellow insoluble residue
3-pic	Dark brown	Blue solution + yellow insoluble residue
2,5-lut	Black	Black-brown solution + yellow insoluble residue
2,6-lut	Black	Black-brown solution
2-pic	Black	Black-brown solution
2,3-lut	Black	Black-brown solution
2,4-lut	Black	Black-brown solution
3,4-lut	Black	Black-brown solution
4-pic	Black	Black-brown solution

influence of the position of the 4-methyl substituent is apparently so marked tha an analogous course of thermal decomposition is observed even in cases when the pyridine ring also has methyl substituents at positions 3 or 2.

As regards the order of the influence of the position of the methyl substituent on the course of the thermal decomposition, division of the compounds into

the above groups shows that position 3 exerts a decisive influence on the thermal decomposition course, even when there is another substituent at position 2. It further shows that position 2 also exerts a specific influence on the thermal decomposition course of the compounds under investigation, but this influence is the weakest of the three.

Our studies to date [1, 4, 8] of the properties of thiocyanatocopper(II) complexes with all isomeric forms of picolines and lutidines show that, though the 2-methyl substituent has the weakest influence on the chemical changes of the NCS groups during the thermal decomposition, it does have a decisive influence on the stereochemical and redox properties of the studied compounds.

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RÉSUMÉ — L'article a trait à l'influence de la position du groupe CH_3 dans les picolines et lutidines, en tant que ligands, sur le degré des changements chimiques des groupes SCN dans les composés de coordination du type $Cu(SCN)_2L_2$ (L = 2-, 3 et 4-picoline, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- et 3,6-lutidine). L'effet le plus prononcé du groupe CH_3 s'observe en position 4. Cette influence du groupe méthyle sur le degré des changements chimiques indique aussi l'influence mutuelle des ligands dans les composés de coordination du Cu(II).

ZUSHMMENFASSUNG — Der Artikel befaßt sich mit dem Einfluß der Lage der CH_3 Gruppe in Pikolinen und Lutidinen als Liganden auf den Grad der chemischen Änderungen der Gruppen NSC in Koordinationsverbindungen des Typs $Cu(NCS)_2L_2$ (L = 2-, 3- und 4-Pikoline, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- und 3,5-Lutidine). Der ausgeprägteste Effekt der CH_3 Gruppe wurde in der Position 4 beobachtet. Dieser Einfluß der Methylgruppe auf das Ausmaß der chemischen Änderungen deutet auch auf die gegenseitige Wirkung der Liganden in Koordinationsverbindungen von Cu(II).

Резюме — Установлено влияние положения метильной группы в пиколинах и лутидинах, как лигандов, на степень химических изменений групп NCS в координационных соединениях типа $Cu(NCS)_2L_2$, где L = 2-, 3- и 4-пиколин, 2.3-, 2.4-, 2.5-, 2.6-, 3.4- и 3.5-лутидин. Найдено, что наиболее ярко выраженное влияние метильной группы проявляется в положении 4. Такое влияние метильной группы на степень химических изменений указывает на совместное влияние лигандов в координационных соединениях Cu(II).