

Preparation and some properties of cyano complexes of the $[M(CN)_5L]^{3-}$ type

J. SKORŠEPA and K. GYÖRYOVÁ

*Department of Inorganic Chemistry, Faculty of Natural Science,
P. J. Šafárik University, CS-041 54 Košice*

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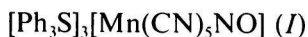
The paper deals with preparation and study of the properties of new cyano complexes of the $[R_3S]_3[M(CN)_5L]$ type ($R = \text{methyl, phenyl}; M = \text{Mn, Cr, Fe}; L = \text{NO, PPh}_3$). The conditions of preparation of these substances have been described in detail, their infrared spectra have been investigated and the basic data about their thermal properties are presented. The results are correlated with the present knowledge concerning the compounds of similar character.

In coherence with literature data [1—4] on some properties of cyano complexes of the $[M(CN)_6]^{3-}$ type containing the $[Ph_2I]^+$ and $[R_3S]^+$ cations, we investigated the preparation of a series of cyano complexes with heterogeneous coordination sphere of the $[M(CN)_5L]^{3-}$ type and with the above-mentioned cations. The aim of this study has been to compare the differences in preparation of these two groups of compounds and to evaluate how the presence of the ligand, *i.e.* NO or PPh_3 affects the properties of cyano complexes. The following group of compounds was prepared and investigated: $[Ph_3S]_3[Mn(CN)_5NO]$ (I), $[Me_3S]_3[Mn(CN)_5NO] \cdot 3H_2O$ (II), $[Me_3S]_3[Cr(CN)_5NO]$ (III), and $[Me_3S]_3[Fe(CN)_5PPh_3] \cdot 3H_2O$ (IV).

Experimental

Anal. grade commercial chemicals were used as starting substances. The compounds containing the tertiary sulfonium cation which were synthesized in laboratory and the silver salt of the corresponding cyano complex [5, 6] were used for preparation of the investigated products.

The composition of these products was confirmed by CHN analysis. The metals were determined complexometrically. The infrared spectra were taken on an instrument Specord M-80 in the region of $\tilde{\nu} = 200\text{—}3600\text{ cm}^{-1}$ by using KBr tablets. The basic parameters of thermal decomposition were measured on a Derivatograph MOM (Budapest) in argon atmosphere up to 900°C .



The aqueous solution of $K_3[Mn(CN)_5NO]$ (1.3 g) was mixed with the aqueous

solution of AgNO_3 (2.8 g) in ammoniacal medium (pH 8—9). The formed light-violet precipitate of $\text{Ag}_3[\text{Mn}(\text{CN})_5\text{NO}]$ was filtered and washed with water. The suspension of $\text{Ag}_3[\text{Mn}(\text{CN})_5\text{NO}]$ (2 g) was added into the aqueous solution of Ph_3SI (3.2 g). The formed yellow precipitate of AgI was filtered off. By concentrating the filtrate a violet product, *i.e.* $[\text{Ph}_3\text{S}]_3[\text{Mn}(\text{CN})_5\text{NO}]$ was separated. The substance was fairly soluble in water, methanol, ethanol, and chloroform. It was insoluble in carbon tetrachloride, benzene, ether, dimethylformamide, and dimethyl sulfoxide. Analytical composition: $w_1(\text{calc.})$: 5.47 % Mn, 70.52 % C, 4.48 % H, 8.36 % N; $w_1(\text{found})$: 5.32 % Mn, 69.82 % C, 4.45 % H, 8.35 % N. The yield was 35—40 %.

$[\text{Me}_3\text{S}]_3[\text{Mn}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$ (II)

The aqueous ammoniacal solution of AgNO_3 (2.4 g, pH 8) was added into the saturated aqueous solution of $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}]$ (1.3 g). A light-violet precipitate of $\text{Ag}_3[\text{Mn}(\text{CN})_5\text{NO}]$ gradually separated. It was filtered and washed with water. $\text{Ag}_3[\text{Mn}(\text{CN})_5\text{NO}]$ (2 g) was added into the aqueous solution of Me_3SI (1.4 g) and the formed yellow precipitate of AgI was filtered off. By concentrating the filtrate the required violet-coloured product was obtained. The substance was fairly soluble in water and methanol and poorly soluble in carbon tetrachloride. It was insoluble in ethanol, chloroform, benzene, ether, dimethylformamide, and dimethyl sulfoxide: Analytical composition: $w_1(\text{calc.})$: 12.26 % Mn, 37.50 % C, 7.36 % H, 15.62 % N; $w_1(\text{found})$: 12.30 % Mn, 35.72 % C, 7.35 % H, 15.59 % N. The yield was 30 %.

$[\text{Me}_3\text{S}]_3[\text{Cr}(\text{CN})_5\text{NO}]$ (III)

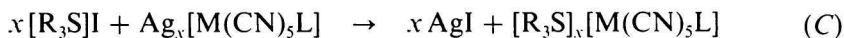
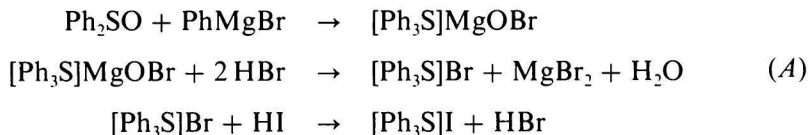
The aqueous ammoniacal solution of AgNO_3 (2.4 g, pH 8.5—9) was added into the aqueous solution of $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}]$ (1.3 g). The gradually arising yellow precipitate of $\text{Ag}_3[\text{Cr}(\text{CN})_5\text{NO}]$ was filtered and washed with water. $\text{Ag}_3[\text{Cr}(\text{CN})_5\text{NO}]$ (2.2 g) was added into the aqueous solution of Me_3SI (1.4 g). The formed yellow precipitate of AgI was filtered off. By concentrating the filtrate the required greenish-brown product came into existence. The prepared compound was soluble in water and poorly soluble in methanol, carbon tetrachloride or ether. It was insoluble in ethanol, chloroform, dimethylformamide, and dimethyl sulfoxide. Analytical composition: $w_1(\text{calc.})$: 11.73 % Cr, 37.92 % C, 6.09 % H, 15.80 % N; $w_1(\text{found})$: 11.58 % Cr, 36.01 % C, 6.08 % H, 15.45 % N. The yield was 45 %.

$[\text{Me}_3\text{S}]_3[\text{Fe}(\text{CN})_5\text{PPh}_3] \cdot 3\text{H}_2\text{O}$ (IV)

The saturated aqueous solution of AgNO_3 (1.1 g) was added into the saturated aqueous solution of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{PPh}_3]$ (1.2 g). A light-yellow precipitate was formed. It was filtered and washed with water. Then the aqueous solution of Me_3SI (0.7 g) was added to $\text{Ag}_3[\text{Fe}(\text{CN})_5\text{PPh}_3]$ (1.3 g) under intensive stirring. The light-yellow precipitate of AgI was filtered off. By concentrating the light-green filtrate the required dark-green product was obtained. The compound was fairly soluble in water, methanol, and carbon tetrachloride. It was insoluble in ethanol, chloroform, benzene, and ether. Analytical composition: $w_1(\text{calc.})$: 8.07 % Fe, 56.56 % C, 6.18 % H, 10.31 % N; $w_1(\text{found})$: 8.05 % Fe, 54.36 % C, 6.15 % H, 10.30 % N. The yield was 40—45 %.

Results and discussion

In spite of some differences in preparation, the investigated compounds exhibit some common characteristic features which can be described by the following equations



The prepared compounds are stable in air and light except the compound that contains iron. The compounds $\text{Ag}_3[\text{Mn}(\text{CN})_5\text{NO}]$ and $\text{Ag}_3[\text{Cr}(\text{CN})_5\text{NO}]$ decompose in acid medium. For this reason, the preparation of these compounds necessitates regulation of the pH value of medium by means of ammonia.

The data of infrared spectra of the prepared substances are listed in Table 1. The strong and medium strong absorption bands of stretching vibrations $\nu(\text{CN})$ of the cyano complexes appear in the region of $\tilde{\nu} = 2045\text{--}2135\text{ cm}^{-1}$ [7].

Other characteristic bands corresponding to components of the investigated compounds occur in equal regions as stated in literature for similar compounds [8, 9]. It is characteristic of the investigated compounds that the NO or PPh_3 ligand is present in the heterogeneous coordination sphere. The NO ligand itself can give bands in different regions of wavelengths according to its character. The observed shifts in absorption bands of individual characteristic vibrations (Table 1) are consistent with the knowledge that the replacement of one cyano group by the NO or PPh_3 ligand results in a shift in the values $\nu(\text{CN})$ of hexacyano complexes towards higher values of wavenumber [10] (compounds *I—III*). But compound *IV* containing iron shows opposite tendency. The values $\nu(\text{CN})$ vary according to the π -acceptor ability of ligands [11]. As the NO group has stronger π -acceptor properties than the PPh_3 ligand, the values $\nu(\text{CN})$ of compound *IV* are lower than those of compounds *I—III* owing to the fact that the reverse π -donation from central atom to the π^* -orbital of cyanide ligand decreases. A shift in values of the wavenumber $\nu(\text{CN})$ by the effect of cation to higher or lower values is due to stabilization of the $\text{C}\equiv\text{N}$ bond (formation of a strong π -bond, resonance structure *A*) while the portion of resonance structure *B* increases by the effect of $d\pi\text{--}p\pi$ metal—ligand interaction and thus the values $\nu(\text{CN})$ shift to lower wavenumbers [12]

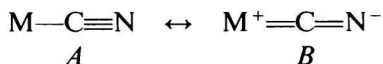
Table 1

Characteristic absorption bands ($\tilde{\nu}/\text{cm}^{-1}$) in infrared spectra of cyano complexes

Compound	Assignment							
	$\nu(\text{C—H})$ (Ph)	$\nu(\text{C—H})$ (Me)	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{NO})$	$\nu(\text{C}=\text{C})$ (Ph)	$\delta(\text{C—H})$ (Me)	$\gamma(\text{C—H})$ (Me)	$\delta(\text{M—CN})$ $\nu(\text{M—CN})$
<i>I</i>	3080 w 3060 w		2120 (sh) 2085 s	1700 s	1480 m 1450 m		745 s 680 s	500 m
<i>II</i>		3025 m	2120 (sh) 2095 vs	1715 vs 1700 (sh)		1430 s 1380 w		470 w 400 m
<i>III</i>		3040 m 2990 w	2135 (sh) 2115 s	1645 vs		1440 s 1375 w		430 m
<i>IV</i>	3060 m	3010 w 3000 w	2060 (sh) 2045 vs 2120 s 2090 w	1725 vs	1480 w	1440 s 1370 s	710 s 690 s	568 m 420 m 481 m 360 w
<i>b</i>			2137 s 2095 (sh) 2121 m	1645 s				459 m 339 m
	3070 w 3055 w		2100 s 2055 s 2095 w		1480 m 1445 m		750 s	570 m 430 w

vs — very strong, s — strong, m — medium, w — weak, sh — shoulder.

a) $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, *b*) $\text{K}_3[\text{Cr}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$, *c*) $\text{Na}_3[\text{Fe}(\text{CN})_5\text{PPh}_3] \cdot 3\text{H}_2\text{O}$.



The values $\delta(\text{M}-\text{CN})$ and $\nu(\text{M}-\text{CN})$ are not sensitive to the presence of ligands.

The principal information about thermal properties of the investigated compounds shows that compound *II* is thermally the least stable among the prepared cyano complex compounds. It starts to decompose at 50 °C. On the other hand, compound *I* is the most stable. It starts to decompose at 200 °C.

The first stage of thermal decomposition of the prepared cyano complex compounds proceeds under endothermic liberation of Me_2S , MeCN , and PPh_3 . The second stage of thermal decomposition involves further liberation of MeCN or PhCN . The final products of thermal decomposition are the sulfides (MnS , FeS) and the carbides of metals (Mn_3C , Cr_3C_2).

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