

CYANO COMPLEXES OF UNIVALENT COPPER WITH SOME PYRIDINE DERIVATIVES

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Dedicated to Professor S. Škramovský on the occasion of his 75th birthday.

Complex compounds of composition $[(LH)Cu_2(CN)_3]$, $[CuLCN]$, and $[L(CuCN)_2]$, where L is pyridine, 2-picoline, 3-picoline, 4-picoline, 2,4-lutidine, 2,5-lutidine, 2,6-lutidine, s-collidine, and methyl or ethyl isonicotines, have been prepared. These compounds are diamagnetic, stable in a crystalline state at room temperature both towards loss of the organic ligand and towards oxidation by air oxygen. For most of them, a polymer structure with a donor-acceptor bonding between the heterocyclic nitrogen atom and copper atom with bridged cyanide groups has been suggested using spectral data.

Cyano complex of univalent copper have been only little mentioned in the literature. The earlier literature^{1,2} refers to unstable complexes of this type with amines or methyl iodide. For structural studies, a more recent reference³ is important that cyano complexes of univalent copper with double-bonded nitrogen ligands, such as phenanthroline or 2,2'-dipyridine, have a polymer structure with tetrahedral arrangement of donor atoms around central copper atoms linked by cyanide bridges. The only one cyanocomplex of univalent copper with pyridine derivatives that has up to now been prepared, is a substance of composition $[Cu(2-pic)_2CN]$ (2-pic denotes picoline), produced by a longer action of 2-picoline on copper(I) cyanide, but it has not been characterized in a more detail⁴. Since we were concerned with halogenides and perchlorates of analogous complexes in previous papers⁵⁻⁸, it was useful to extend this group of substances also for cyanides and to compare their constitution and kind of bonding between one another.

EXPERIMENTAL

Organic ligands were purified chromatographically, the other reagents (A.R. grade) were products of firm Lachema.

Copper was determined gravimetrically as $CuSCN$; carbon, hydrogen, and nitrogen were established by elementary organic analysis. IR spectra in the region of $400-4000\text{ cm}^{-1}$ were made using spectrophotometer UR-20 (Zeiss, Jena). Samples of solid compounds were treated with the nujol mull or KBr disc techniques.

The reflection spectra of solid compounds were measured with use of apparatus VSU-1 (Zeiss, Jena) in a mixture with MgO which also served as standard.

Magnetic susceptibilities were measured on a torsion magnetic balance⁹ by the Faraday method. The X-ray patterns were achieved by the powder method using Mikrometa 2 apparatus (\varnothing 57.3 mm, $\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$).

The complexes were prepared by reduction with ascorbic acid from water or water-alcoholic solutions of the ligand with copper(II) sulphate in various molar ratios. An aqueous solution of potassium cyanide was added to the reduced solution. The precipitated cyanides were filtered off, washed several times with water and dried at room temperature.

RESULTS

Composition of the final product depends on concentration ratios of ligand, copper, and cyanide, and on the composition of the solvent. The composition and analysis of the compounds obtained, as well as frequency of important vibrations of the CN group, are summarized in Table I. It follows from this Table that for 2-picoline, 3-picoline, and 4-picoline two compounds, and for pyridine three compounds, all of different stoichiometry, could be prepared. As regards the $[\text{Cu}(2\text{-pic})_2\text{CN}]$ compound mentioned in the literature⁴, it is produced only by a longer reaction in non-aqueous solution, and has not been studied by us.

The compounds obtained are all diamagnetic and stable at room temperature both towards oxidation by air oxygen and towards release of organic ligand. Whereas, for example, the component of composition $[\text{Cu}(\text{NH}_3)\text{CN}]$ loses NH_3 within 3 days already¹⁰, the composition and structure of the compounds prepared by us has not changed even after one year. The compounds prepared by us are insoluble in common solvents and could not therefore be studied in solutions. The $[\text{Cu}(\text{MeIN})\cdot\text{CN}]$ and $[\text{Cu}(\text{EtIN})\text{CN}]^*$ compounds are of yellow colour, all the other compounds presented in Table I are colourless.

The reflection spectra of both yellow compounds have a band of the charge transfer $\text{Cu} \rightarrow \text{L}$ at 420 nm, analogously to other compounds of this type^{7,8}.

Interplanar distances achieved by the X-ray method give evidence both of chemical individuality of the compound studied, and of the fact that no couple of them is isomorphous.

DISCUSSION

Comparison of IR spectra of free and coordinated ligands shows the molecules of all the studied pyridine derivatives to be single-bonded ligands coordinated to Cu(I) by means of heterocyclic nitrogen. The shifts of the IR spectra bands, which give evidence of that fact, are quite analogous to those described in previous papers for univalent copper^{5,7,8} as well as for complexes of other metals^{11,12}.

* Meaning of symbols see Table I.

TABLE I

Analyses and Valence Vibrations of the CN Group of Studied Compounds

Abbreviations: py pyridine, pic picoline, lut lutidine, s-coll symmetric collidine, MeIN and EtIN methyl and ethyl isonicotinates, w weak, m medium, s intensive, v very.

| Compound | Analytical composition, % found/% calculated | | | | ν CN, cm^{-1} |
|--|---|----------------|--------------|----------------|--------------------------------|
| | Cu | C | H | N | |
| [Cu(py)CN] | 38.02 37.68 | 41.91 42.13 | 2.97 2.99 | 16.30 16.60 | 2 130 ms, 2 110 wm 2 085 ms |
| [Cu(3-pic)CN] | 34.54 34.78 | 45.88 46.02 | 3.82 3.86 | 15.04 15.32 | 2 130 ms, 2 120 m 2 085 ms |
| [Cu(2-pic)CN] | 34.23 34.78 | 45.59 46.02 | 3.68 3.86 | 15.23 15.32 | 2 138 vs |
| [Cu(4-pic)CN] | 35.09 34.78 | 45.67 46.02 | 3.56 3.86 | 15.15 15.32 | 2 135 vs |
| [Cu(2,4-lut)CN] | 32.25 32.30 | 48.34 48.80 | 4.55 4.61 | 14.28 14.23 | 2 138 vs |
| [Cu(2,5-lut)CN] | 32.63 32.30 | 48.44 48.80 | 4.36 4.61 | 14.54 14.23 | 2 138 vs |
| [Cu(2,6-lut)CN] | 32.02 32.30 | 48.35 48.80 | 4.51 4.61 | 14.04 14.23 | 2 138 vs |
| [Cu(s-coll)CN] | 30.38 30.16 | 50.88 51.30 | 5.27 5.26 | 13.00 13.28 | 2 135 vs |
| [Cu(MeIN)CN] | 27.98 28.03 | 41.98 42.38 | 2.97 3.11 | 11.92 12.35 | 2 140 s |
| [Cu(EtIN)CN] | 26.49 26.40 | 44.19 44.91 | 3.78 3.77 | 11.46 11.63 | 21,32 ms |
| [(py).(CuCN) ₂] | 48.83 49.21 | 33.04 32.56 | 2.04 1.95 | 16.32 16.26 | 2 170 m, 2 150 vs |
| [(2-pic).(CuCN) ₂] | 46.39 46.68 | 35.81 35.29 | 2.80 2.59 | 15.15 15.42 | 2 170 w, 2 125 vs |
| [(4-pic).(CuCN) ₂] | 46.93 46.68 | 35.00 35.29 | 2.55 2.59 | 15.29 15.42 | 2 170 m, 2 145 vs |
| (pyH).[Cu ₂ (CN) ₃] | 44.28 44.55 | 33.51 33.68 | 2.14 2.12 | 20.05 19.64 | 1 130 vs |

As to the kind of the bonding of cyanide groups, a conclusion may be drawn from the position and number of bands of valence vibrations of the CN group in the vicinity of 2100 cm^{-1} (Table I). In compounds of the $[\text{CuL}(\text{CN})]$ type only one sharp and intensive band in the region of $2130\text{--}2140\text{ cm}^{-1}$ mostly appears; for compounds $[\text{Cu py}(\text{CN})]$ and $[\text{Cu}(3\text{-pic})\text{CN}]$ only, 3 bands for each, of medium intensity in the region of $2085\text{--}2130\text{ cm}^{-1}$, may be observed. As has been confirmed by the literature data^{13,14}, the valence vibration of bridged cyanide groups has a greater wave number than valence vibration of the terminal cyanide groups. For example¹⁵, compound $\text{K}_3[\text{Cu}(\text{CN})_4]$ whose anion is of the T_d symmetry, has only terminal cyanide groups coordinated through the cation atom, and their vibrations lie at $2075\text{--}2095\text{ cm}^{-1}$ [ref.¹⁶] in the IR spectra. Unlike this, the $[\text{Cu}(\text{L—L})\text{.CN}]$ complexes, where L—L is fenanthroline or 2,2'-dipyridine, have a polymer structure with exclusively bridged cyanide groups³ and are noted for only one sharp and intensive band at 2100 or 2105 cm^{-1} , respectively. For that reason, also those of the $[\text{CuL}(\text{CN})]$ type complexes studied by us, which have only one band of the CN group at frequencies higher than 2130 cm^{-1} , are probably of a polymer structure with double-bonded bridged CN groups.

In contrast to this group of compounds, the substances of composition $[\text{Cu}(\text{py})\text{CN}]$ and $[\text{Cu}(3\text{-pic})\text{CN}]$ have the valence vibrations of the CN group split into 3 bands in the region of $2085\text{--}2130\text{ cm}^{-1}$. Splitting of this vibration into 2 bands at 2085 and 2105 cm^{-1} was found for compound $\text{K}[\text{Cu}(\text{CN})_2]$ the anion of which is of polymer nature and has a shape of a spiral chain with bridged and terminal CN groups¹⁷. The splitting of the vibration of the CN group into 3 bands within $2065\text{--}2130\text{ cm}^{-1}$ was found for compound $[\text{Cu}(\text{NH}_3)\text{CN}]$ which has a structure composed from layers of polymerized CuCN groups among which the NH_3 molecules are situated [ref.¹⁸]. It is therefore probable that also the $[\text{Cu}(\text{py})\text{CN}]$ and $[\text{Cu}(3\text{-pic})\text{CN}]$ compounds are polymerized and have both double-bonded bridged CN groups and single-bonded end CN groups. For these two compounds, ionic structure $[\text{CuL}_2]^+[\text{Cu}(\text{CN})_2]^-$ with a polymerized anion cannot be excluded owing to the analogy with the $\text{K}[\text{Cu}(\text{CN})_2]$ compound.

The vibration frequency of the CN group can be also affected by the coordination number of central Cu(I) ion. A greater number of coordinated groups around the Cu(I) ion makes¹⁹ the negative charge to increase on it and the electron density is therefore shifted from Cu(I). As a result of this, also wave number of the CN group decreases. Since the already mentioned complexes with double-bonded ligands, phenanthroline and 2,2'-dipyridine, of composition $[\text{Cu}(\text{L—L})\text{CN}]$ (I) have the Cu(I) ion 4 time coordinated³ and the νCN bands at 2100 and 2105 cm^{-1} , complexes $[\text{CuL}(\text{CN})]$ (II) with one νCN band above 2130 cm^{-1} , studied by us, can be assumed to have the coordination number lower, *i.e.* 3 and structure



with bridged CN groups.

The ionic structure of the $[\text{CuL}_2]^+ \cdot [\text{Cu}(\text{CN})_2]^-$ type is not probable in these compounds, as follows from comparison of the IR spectra of free ligand L, cyanide $[\text{CuL}(\text{CN})]$, and perchlorate $[\text{CuL}_2](\text{ClO}_4)$. For perchlorates of this type, in which L is 4-picoline, 3 different lutidines, and s-collidine, ionic structure $[\text{CuL}_2]^+ \cdot [\text{ClO}_4]^-$ [ref.7] has been proved. If cyanides $[\text{CuL}(\text{CN})]$ had cations analogous to those of perchlorates $[\text{CuL}_2](\text{ClO}_4)$, the wave numbers of various vibrations of the pyridine nucleus would have to be in accordance for cyanides as well as perchlorates. The results show that the shift of wave numbers of various vibrations of the ligand^{20,21} towards higher values, as a consequence of its coordination to Cu(I), is lower for cyanides than for perchlorates and the difference is evident particularly with vibrations at lower wave numbers.

Compounds of the $[\text{CuL}(\text{CN})]$ type, where L is 2-picoline, 4-picoline, 2,4-lutidine, 2,5-lutidine, 2,6-lutidine, s-collidine, and methyl or ethyl isonicotinate, may be then assumed to have a polymer nonionic structure with the bridged CN groups only and three times coordinated copper atoms. The yellow colour of compounds $[\text{Cu}(\text{MeIN})\text{CN}]$ and $[\text{Cu}(\text{EtIN})\text{CN}]$ and the corresponding band of the charge transfer $\text{Cu} \rightarrow \text{N}$ at 420 nm in the reflection spectra can be explained by the fact that substituents $-\text{COOCH}_3$ and $-\text{COOC}_2\text{H}_5$ are for these two ligands on the pyridine nucleus considerably more negative than in case of the other ligands and therefore make easier the charge transfer from metal to ligand. The yellow colour gives also evidence of the fact that these compounds have no ionic structure, because ionic perchlorates $[\text{Cu}(\text{MeIN})_2]^+ (\text{ClO}_4)^-$ and $[\text{Cu}(\text{EtIN})_2]^+ (\text{ClO}_4)^+$ are white⁷.

The compounds of equal type, *i.e.* $[\text{CuL}(\text{CN})]$, in which L is either pyridine or 3-picoline, are probably of polymer nature with bridged as well as terminal CN groups, and the ionic structure of the $[\text{CuL}_2]^+ \cdot [\text{Cu}(\text{CN})_2]^-$ type cannot be here excluded. Perchlorates of composition $[\text{Cu}(\text{py})_2]\text{ClO}_4$ and $[\text{Cu}(\text{3-pic})_2]\text{ClO}_4$ have not been known hitherto and an analogous comparison of IR spectra, as in case of the preceding group of substances, cannot be therefore accomplished.

As regards the 3 compounds of the $[\text{L}(\text{CuCN})_2]$ type, likewise polymer structure with bridged cyanide groups and with a coordination number of copper lower than 4 may be assumed in these substances for the reasons mentioned in the discussion.

Compound $[(\text{pyH})\text{Cu}_2(\text{CN})_3]$ is probably pyridinium salt, owing to the present bands at 3200, 1540, 1325, 1250, and 668 cm^{-1} in its IR spectrum, which can be attributed to $\nu\text{N}-\text{H}$ vibrations^{22,23} and which were not observed in the spectra of compounds $[(\text{py})(\text{CuCN})]$ and $[(\text{py})(\text{CuCN}_2)]$. Its anions $[\text{Cu}_2(\text{CN})_3]^-$ are

obviously of polymer character with bridged double-bonded CN groups and with coordination number 3 on the Cu(I) atom.

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