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# Pseudotetrahedral Cobaltate(II) Anions with Two and Three Different Kinds of Ligands

## Short Communication

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New complexes of the general types $HCo(NCS)_3 \cdot nL$, $HCoX_2(NCS) \cdot nL$ and $HCo(NCS)_2I \cdot nL$ (where $X = Cl$, Br, I; $L =$ diethyl ether, pyridine, aniline; $n = 1.5$, 2, 3, 3.5) have been prepared and characterized. The magnetic and spectroscopic data indicate that pseudotetrahedral $[Co(NCS)_3L]^-$, $[CoX_2(NCS)L]^-$ and $[Co(NCS)_2IL]^-$ anions are present in the solid pyridine and aniline compounds.

*[Keywords: IR spectra; Ligand field spectra; Magnetic moments; Pseudotetrahedral cobaltate(II) anions]*

*Pseudotetraedrische Kobaltat(II)-Anionen mit zwei bzw. drei verschiedenartigen Liganden (Kurze Mitteilung)*

Neue Komplexe der allgemeinen Formeln $HCo(NCS)_3 \cdot nL$, $HCoX_2(NCS) \cdot nL$ und $HCo(NCS)_2I \cdot nL$ (wobei $X = Cl$, Br, I; $L =$ Diethylether, Pyridin, Anilin; $n = 1{,}5$, 2, 3, 3,5) wurden dargestellt und charakterisiert. Die magnetischen und spektroskopischen Ergebnisse weisen darauf hin, daß in den festen Pyridin- und Anilin-Komplexen pseudotetraedrische $[Co(NCS)_3L]^-$-, $[CoX_2(NCS)L]^-$- und $[Co(NCS)_2IL]^-$-Anionen vorliegen.

## Introduction

Complexes containing the monomeric pseudotetrahedral anions $[CoX_3L]^-$ or $[CoX_2YL]^-$ ($X$, $Y$ = halogens or pseudohalogens; $L$ = a monodentate neutral ligand) are quite rare[1-4]. The present communication describes some new etherate, pyridine and aniline compounds of simple and mixed pseudohalo- and haloacids of Co(II). The compounds

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chosen may be regarded as model systems for the above-mentioned anions.

## Results and Discussion

The complexes were prepared, in ca. 75–90% yields, by previously described methods[5–8]. Physicochemical and spectroscopic measurements were carried out as previously reported[5,7,9]. All the complexes gave satisfactory elemental analyses.

For all four Co(II) halides and thiocyanates, resp., the oily proton acids $HCoX_2(NCS)\cdot 2\,Et_2O$ ($X = Cl, I$), $HCoBr_2(NCS)\cdot 3\,Et_2O$, $HCo(NCS)_3\cdot 3.5\,Et_2O$ and $HCo(NCS)_2I\cdot 1.5\,Et_2O$, where $Et_2O$ = diethyl ether, have been isolated.

The pyridine and aniline compounds are formed by the complete displacement of the ether molecules in the etherates with pyridine or aniline. They are crystalline solids, stable in air, insoluble in nonpolar solvents, soluble in alcohols, acetone, $CH_3NO_2$, *DMF* and *DMSO*. They are decomposed by dilute mineral acids. The X-ray powder patterns show them to be isomorphous with the corresponding pseudotetrahedral Zn(II) complexes[5,7]. Table 1 gives some important features of the solid compounds. From the $\Lambda_M$ values obtained it is concluded that they behave in $CH_3NO_2$ as 1 : electrolytes[10].

A pseudotetrahedral configuration is assigned to all the solid complexes on the basis of their magnetic moments and visible diffuse

Table 1. *Colors, decomposition temperatures, $\Lambda_M$ values, magnetic moments, pyridine and*

| *Complex* | *Color* | *Dec. temp.* (°C) | $\Lambda_M^a$ ($S\,cm^2mol^{-1}$) | $\mu_{eff}^b$ (B.M.) |
|---|---|---|---|---|
| $HCo(NCS)_3\cdot 3\,Py$ | dark blue | 141–146 | 80 | 4.41 |
| $HCo(NCS)_3\cdot 3\,An$ | dark blue | 127–132 | 86 | 4.46 |
| $HCoCl_2(NCS)\cdot 3\,Py$ | deep blue | 113–117 | 77 | 4.45 |
| $HCoCl_2(NCS)\cdot 3\,An$ | deep blue | 106–110 | 79 | 4.52 |
| $HCoBr_2(NCS)\cdot 3\,Py$ | deep blue | 118–122 | 82 | 4.54 |
| $HCoBr_2(NCS)\cdot 3\,An$ | deep blue | 120–125 | 73 | 4.62 |
| $HCoI_2(NCS)\cdot 3\,Py$ | dark green | 130–135 | 96 | 4.66 |
| $HCoI_2(NCS)\cdot 3\,An$ | dark green | 123–128 | 84 | 4.75 |
| $HCo(NCS)_2I\cdot 3\,Py$ | blue-green | 105–110 | 126 | 4.60 |
| $HCo(NCS)_2I\cdot 3\,An$ | blue-green | 110–116 | 90 | 4.73 |

[a] Values of molar conductance for ca. $10^{-3}\,M$ solutions in $CH_3NO_2$ at 25 °C.
[b] At room temperature.
[c] Assuming $C_{3v}$ symmetry.

reflectance spectra[1, 3, 4]. The typical symmetry of the metal-ligand environment in $HCo(NCS)_3 \cdot 3\,L$ ($L$ = pyridine, aniline) is approximately $C_{3v}$ and even lower ($C_s$) in those cases where both halide and isothiocyanate ions are coordinated. The trend of the $\mu_{eff}$ values, increasing in the sequence NCS < Cl < Br < I, is consistent with an increasing contribution to the spin-only value as the ligand field strength of these anions decreases[1]. The complex maximum near 650 nm in the solid state electronic spectra is basically associated with what would be a $^4A_2(F) \rightarrow {}^4T_1(P)$ transition for species of full tetrahedral symmetry. The complexity of this band has been attributed to spin-orbit coupling effects, but in the present case splitting would also be expected because of the reduction of the symmetry. The spectra of the complexes $HCo(NCS)_3 \cdot 3\,L$ and $HCoX_2(NCS) \cdot 3\,L$ with the same organic ligand are fairly similar. Assignment of the spectra of $HCoX_2(NCS) \cdot 3\,L$ and $HCo(NCS)_2I \cdot 3\,L$ on the basis of a $C_{3v}$ symmetry, instead of an expected $C_s$ symmetry[4], is therefore tolerable.

The solid pyridine and aniline complexes have IR spectra (4000–250 cm$^{-1}$) indicative of the presence of coordinated organic base and of the existence of $[L_2H]^+$ counterions[5, 7]. The NCS group is coordinated via the N-atom, since $\nu(C{\equiv}N)$ and $\delta$(NCS) are observed in the regions expected for N-coordination[5, 9]; the appearance of the $\nu(C{\equiv}N)$ band at 2080 cm$^{-1}$ indicates the absence of bridged —SCN— groups or ionic thiocyanates. The positions of $\nu(Co{-}X)_t$ and $\nu$(Co—NCS) bands

*diagnostic visible diffuse reflectance maxima (nm) and far IR data (cm$^{-1}$) of the aniline complexes*

| $^4A_2(F) \rightarrow {}^4A_2(T_1, P)$, $^4E(T_1, P)^c$ | $\nu(Co{-}X)_t^d$ | $\nu(Co{-}NCS)^d$ | $\nu(Co{-}L)^d$ |
|---|---|---|---|
| 614, 599 sh, 587 sh | | 312 s, 291 s | 228 sh, 193 m |
| 607, 594 sh, 588 sh | | 310 m, 294 m | 416 m, 361 s |
| 654, 645 sh, 626 sh | 316 sb$^e$, 306 s | 316 sb$^e$ | 234 m, 199 w |
| 643 sh, 630 | 314 sb$^e$, 301 s | 314 sb$^e$ | 412 m, 358 m |
| 689 sh, 670, 643 sh | 256 sh, 239 s | 312 s | 234 sh, 196 m |
| 676 sh, 665, 628 sh | 254 sh, 237 s | 315 m | 418 m, 361 s |
| 719, 683 sh, 640 sh | 211 s, 201 mb$^e$ | 310 s | 233 sh, 201 mb$^e$ |
| 707, 671 sh, 648 sh | 211 sh, 199 s | 308 s | 412 m, 351 s |
| 688, 654, 619 sh | 214 m | 303 s, 287 m | 236 m, 203 m |
| 679, 624 sh | 211 m | 299 m, 284 m | 411 m, 350 m |

[d] From Refs. [2–4, 11, 12].
[e] Overlapping.

distinguish between an individual complex and mixtures of other related forms[2].

On the basis of the overall study presented, the formulae $[L_2H]^+[Co(NCS)_3L]^-$, $[L_2H]^+[CoX_2(NCS)L]^-$ and $[L_2H]^+[Co(NCS)_2IL]^-$ are proposed for the complexes in the solid state; the anions possess pseudotetrahedral configurations.

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