Crystallographic and Spectroscopic Evidence of O-Bonding in 3d-Metal Dicyanomethanidonitrite Complexes

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Dicyanomethanidonitrite Complexes

The coordination of the dicyanomethanidonitrite group through the nitroso oxygen atom in the tetrakis(pyridine) complexes \([\text{M(O\text{NC}(\text{CN})_2)\text{(py)}_4]}\), \(\text{M} = \text{Ni, Co, Cu}\), and in the bis(pyridine) complex \([\text{Cu(O\text{NC}(\text{CN})_2\text{(py)}_2)]}\) was proved by X-ray crystallography of the Ni\text{II} complex and re-evaluated infrared spectra. The Ni\text{II} and Co\text{II} complexes exhibit almost octahedral structures composed of four pyridine nitrogen atoms and two oxygen atoms of the dicyanomethanidonitrite ions. Both copper(II) complexes display a considerable axial distortion of the pseudo-octahedral arrangement. In the bis(pyridine) Cu\text{II} complex the ONC(CN)\text{II} groups are involved in the bridging function by use of the oxygen and nitrile nitrogen atoms.

Introduction

The dicyanomethanidonitrite anion \([\text{ONC}(\text{CN})_2]\) is a typical ambidentate ligand, the coordination of which can be realized through its nitroso or nitrile nitrogen, or oxygen atoms. Complexes of this anion have only a small tendency to form single crystals and therefore, the bonding modes of \([\text{ONC}(\text{CN})_2]\) were prevalently determined by means of infrared data [1–6]. From these results the general conclusion was drawn, that in the complexes of \(d\)-metals the ONC(CN)\text{II} group is bonded by means of the nitroso nitrogen atom [2,7–10]. However, complexes containing neutral organic ligands exhibit many bands in the middle-IR region corresponding to these ligands, and the assignment of the dicyanomethanidonitrite bands cannot be always unambiguous.

In the last years a number of crystal structures of dicyanomethanidonitrite complexes with \(3d\) metals were solved and the coordination of the anionic ligand through oxygen was determined [6,11–14]. In order to bring more light into these circumstances, we prepared a group of pyridine complexes, the infrared spectra of which served Köhler et al. [1–3] to determine the bonding mode of this group in \(3d\)-metal complexes. Single crystals of \([\text{Ni(O\text{NC}(\text{CN})_2\text{(py)}_4]}\) (py = pyridine) were obtained and the structure solved by X-ray crystallography. A spectroscopic investigation of this compound together with analogous Co\text{II} and Cu\text{II} tetrakis(pyridine) complexes and a Cu\text{II} bis(pyridine) complex was also undertaken and the assignment of the dicyanomethanidonitrite IR bands was re-evaluated.

Experimental Section

Preparation and analysis

The complexes under study were prepared according to Köhler and Seifert [1] and obtained in microcrystalline state. Single-crystals of \([\text{Ni(O\text{NC}(\text{CN})_2\text{(py)}_4]}\) used for X-ray crystallography were obtained by recrystallisation of the powder sample. The powder sample was dissolved in a hot mixture of isopropanol with 10% of acetonitrile. Small single crystals deposited from the solution.
The complexes were analysed for metal by che-
latometry after decomposition by the action of 
H₂SO₄ and K₂S₂O₈. Elemental analyses were car-
ried out using a Carlo-Erba C, H, N analyser.
Found contents were in satisfactory agreement 
with the calculated values.

X-ray crystallographic analysis

The X-ray diffraction data of 
[Ni{ONC(CN)₂}₂(py)₄] were collected at room 
temperature, on a Nonius B.V. MACH3 four-circle 
diffractometer using Cu-Kα radiation (λ = 
1.54178 Å) from a rotating anode generator (Non-
lius B.V. FR591 Model) equipped with a graphite 
monochromator. The independent reflections 
were measured in the ω/2θ-scan mode in the 5– 
62° θ range. Unit cell parameters were determined 
by least-squares refinement of the setting angles 
of 25 high-angle reflections (25° < θ < 35°). During 
the data collection, three standard reflections were 
measured periodically to monitor misalignment, 
crystal decay or electronic instability. Their inten-
sities showed only small random variations. The 
intensities were corrected for Lorentz and polar-
ization effects, but no absorption correction was 
applied. The main crystallographic data are given 
in Table 1.

The crystal structure was solved by the Patterson 
method and subsequent Fourier synthesis using a 
SHELXS86 [15]. Refinement was made by full-ma-
trix least-squares SHELXL93 software [16] to a 
R(F) value of 0.0674. Non-hydrogen atoms were 
treated anisotropically, hydrogen atom positions 
were located from difference maps and constrained 
(pyridine C–H = 0.93 Å with U(H) = 1.2Ueq of C). Tables of non-hydrogen atom parameters, anisot-
ropic thermal parameters, complete lists of bond 
lengths and angles, as well as measured and calcu-
lated structure factors for the structure of 
[Ni{ONC(CN)₂}₂(py)₄] have been deposited at the 
Cambridge Crystallographic Data Centre, E-mail: 
deposit@ccdc.cam.ac.uk deposition code 148850.

Physical measurements

IR spectra were recorded from KBr pellets (4000–400 cm⁻¹) and Nujol mulls (400–100 cm⁻¹) 
using a Nicolet FT-IR Magna 750 spectrometer. 
UV-Vis-near IR spectra of the solid samples were 
measured on Specord 200, Analytical Jena and 
Perkin Elmer Lambda 19 instruments.

The stoichiomtery of thermal decomposition 
was studied using a MOM derivatograph. In all 
thermal decompositions a sample mass of 100 mg

Table 1. Crystallographic data for 
[Ni{ONC(CN)₂}₂(py)₄]a

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Ni{ONC(CN)₂}₂(py)₄]</th>
</tr>
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<tbody>
<tr>
<td>Formula</td>
<td>NiC₂H₂N₁₀O₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>563.23</td>
</tr>
<tr>
<td>Crystal system/Space group</td>
<td>orthorhombic/Pccn</td>
</tr>
<tr>
<td>a [Å]</td>
<td>10.090(2)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>17.304(3)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>16.779(2)</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>2929.6(8)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>D(calc) [g cm⁻³]</td>
<td>1.277</td>
</tr>
<tr>
<td>Crystal size [mm³]</td>
<td>0.078×0.121×0.157 mm³</td>
</tr>
<tr>
<td>Instrument</td>
<td>Nonius B.V. MACH3</td>
</tr>
<tr>
<td>μ (Cu–Kα [mm⁻¹])</td>
<td>1.290</td>
</tr>
<tr>
<td>Temperature [K]</td>
<td>293(2)</td>
</tr>
<tr>
<td>θ Range [°]</td>
<td>5.07–61.85</td>
</tr>
<tr>
<td>Scan mode</td>
<td>ω/2θ</td>
</tr>
<tr>
<td>Crystal decay</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Unique reflections</td>
<td>2303</td>
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<tr>
<td>Reflections observed</td>
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<tr>
<td>Absorption corrections applied</td>
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</tr>
<tr>
<td>Residuals: R(F²)</td>
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</tr>
<tr>
<td>wR(F²)</td>
<td>0.0610</td>
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<tr>
<td>GOF</td>
<td>0.991</td>
</tr>
<tr>
<td>Parameters refined</td>
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</tr>
<tr>
<td>Weighting scheme</td>
<td>1/σ²(F²)+(0.0127P)²</td>
</tr>
<tr>
<td>Residual electron density [e Å⁻³]</td>
<td>−0.22/0.24</td>
</tr>
</tbody>
</table>

a P = [Max (F₀, 0) + Fc²] / 3

was used and the rate of temperature increase was 
6 °C min⁻¹.

Results and Discussion

Thermal properties

The TG and DTG curves show that 
[Ni{ONC(CN)₂}₂(py)₄] at 55 °C releases one mole of 
pyridine, at 150 °C the remaining three moles of 
the volatile ligand escape; at 310 °C a total de-
composition begins.

The thermal decomposition of 
[Co{ONC(CN)₂}₂(py)₄] begins at 140 °C when two 
moles of pyridine are released. At 175 °C a total 
decomposition occurs with formation of a cobalt 
oxide.

The compound [Cu{ONC(CN)₂}₂(py)₄] when 
heated to 70 °C loses one mole of pyridine and 
at 155 °C the remaining pyridine is released. At 
400 °C total decomposition takes place and CuO is 
formed.

The thermal decomposition of 
[Cu{ONC(CN)₂}₂(py)₄] begins at 140 °C with re-
lease of one mole of pyridine. Loosening the second
pyridine ligand, the complex is continually decomposed and from 450 °C it is transformed into CuO.

Description of the structure of
\[\text{[Ni(ONC(CN)₂)₂(py)₄]}\]

The crystal structure of \[\text{[Ni(ONC(CN)₂)₂(py)₄]}\] consists of discrete molecules, in which the Ni atom in special 4c position is surrounded by four nitrogen atoms [two at 2.099(5) and two at 2.136(5) Å] and by two oxygen atoms [at 2.043(4) Å]. The nickel(II) environment is a slightly deformed octahedron (Fig. 1), composed of four nitrogen atoms of the pyridine ligands and two oxygen atoms of the nitrosodicyanomethanide anions. Interatomic distances and angles are given in Table 2. The molecules in the crystal structure are held together mainly by van der Waals contacts, hydrogen bonds are not important.

Infrared spectra

The bonding mode of the ONC(CN)₂ groups is most expressively reflected in the \(v_{\text{as}}(\text{ONC})\) and \(v_\text{s}(\text{ONC})\) modes. Köhler et al. pointed out [2,3,7] that in the case of the coordination of this group through the nitroso nitrogen atom both modes are significantly shifted to higher frequencies in comparison with the frequencies of the free anion. On the other hand if the dicyanomethanidonitrite is coordinated via oxygen, \(v_{\text{as}}(\text{ONC})\) is shifted to higher frequencies but \(v_\text{s}(\text{ONC})\) to lower ones as compared with the free anion values. In the latter case it can be stated that the \(v_{\text{as}}\) mode contains prevalingly the \(\nu(C=N)\) vibration, while the \(v_\text{s}\) mode involves mainly the \(\nu(N-O)\) vibration.

On the basis of these criteria Köhler and Seifert presumed that in the compounds \[\text{[M(ONC(CN)₂)₂(py)₄]}\] (\(M = \text{Ni, Co, Cu}\)) and \[\text{[Cu(ONC(CN)₂)₂(py)₂]}\] the dicyanomethanidonitrite is coordinated through the nitroso nitrogen atom. This is not in agreement with the crystal structure of the nickel(II) compound. The mentioned authors based their assumptions on the incorrect assignment of the \(v_{\text{as}}(\text{ONC})\) modes. This is not surprising in view of the presence of many pyridine bands in the relevant region.

The new assignment of the dicyanomethanidonitrite bands is shown in Table 3. It can be seen that for the nickel(II) and cobalt(II) complexes the \(v_{\text{as}}(\text{ONC})\) and \(v_\text{s}(\text{ONC})\) modes are shifted by ca. 60 and 30 cm\(^{-1}\) to higher and lower frequencies, respectively, as compared with the values of KONC(CN)₂. This situation is consistent with oxygen bonding of the dicyanomethanidonitrite which was proved crystallographically for the nickel(II) compound. In older papers [3] the \(v_{\text{as}}(\text{ONC})\) component at \(\approx 1350\) cm\(^{-1}\) was assigned to \(v_\text{s}(\text{ONC})\), while the band at \(\approx 1250\) cm\(^{-1}\) was not taken into consideration. The band at \(\approx 1380\) cm\(^{-1}\) can also be assigned to \(v_{\text{as}}(\text{ONC})\).

Examples of the compounds in which the oxygen coordination of dicyanomethanidonitrite to a transition metal was established by X-ray crystal-

| N1—N2 | 2.099(5) | N2—N1—N8 | 89.4(2) |
| N1—N2' | 2.099(5) | N2—N1—N2' | 93.2(3) |
| N1—N8 | 2.093(2) | N2—N1—O14 | 94.9(2) |
| N1—O14 | 2.043(4) | N8—N1—O14 | 87.2(2) |
| O14—N15 | 1.288(5) | N1—O14—N15 | 125.2(4) |
| N15—C16 | 1.304(6) | O14—N15—C16 | 114.3(5) |
| C16—C17 | 1.434(8) | N15—C16—N17 | 117.9(7) |
| C16—C19 | 1.415(8) | N15—C16—N19 | 123.6(6) |
| C17—N18 | 1.140(7) | C16—C17—N18 | 179.8(8) |
| C19—N20 | 1.154(7) | C16—C19—N20 | 176.8(9) |

D—H···A  D—H H···A  D···A  D—H···A
C9—H9···O14  0.930(11)  2.461(8)  2.966(8)  114.2(7)
C7—H7···N15'  1.080(5)  2.559(8)  3.129(7)  120.0(6)
C13—H13···O14  0.930(11)  2.492(8)  2.949(8)  110.4(8)

* Symmetry code used: (i) 1/2-x, 1/2-y, z.
lography are \([\text{Cu}\{\text{ONC}(\text{CN})_2\}_2(\text{1-meiz})_4]\) (meiz = methylimidazole) [6] and \([\text{Ni}\{\text{ONC}(\text{CN})_2\}_2(\text{pz})_4]\) (pz = pyrazole) [11]. In the former compound, which has the coordination geometry of an elongated octahedron with oxygen atoms from \([\text{ONC}(\text{CN})_2]^-\) anions in apical sites (Cu–O = 2.537 Å), both \(v(\text{ONC})\) frequencies are only little changed in comparison with the respective free ion frequencies. On the other hand, the latter compound of practically octahedral donor arrangement exhibits bands at 1386 and 1361 cm\(^{-1}\) which can be assigned to the \(v_\text{as}(\text{ONC})\) modes and a band at 1255 cm\(^{-1}\) assignable to the \(v_\text{s}(\text{ONC})\) mode. These data very well correspond with those for \([\text{M}\{\text{ONC}(\text{CN})_2\}_2(\text{py})_4]\) complexes (M = Ni, Co).

From this point of view the infrared spectra of a series of other dicyanomethanidinitrite complexes of Ni\(^{II}\), Co\(^{II}\) and Cu\(^{II}\) [4–6] were re-assigned and the conclusion was made that in all these compounds dicyanomethanidinitrite groups are bonded via oxygen.

Unlike dicyanamide and tricyanomethanide compounds, the bonding mode of dicyanomethanidinitrite does not show a distinct influence on the \(v(\text{C}=\text{N})\) values. Therefore the bridging function of dicyanomethanidinitrite in \([\text{Cu}\{\text{ONC}(\text{CN})_2\}_2(\text{py})_2]\) through oxygen and nitride nitrogen (see electronic spectra) is not manifested according to the foregoing observations [6].

The far IR spectra (400–100 cm\(^{-1}\)) show three or four absorptions in the region 315–255 cm\(^{-1}\) which can be assigned to the skeletal stretching M–donor atom modes. The bands between 280 and 250 cm\(^{-1}\) very likely can be assigned to the M–N(py) stretches, which usually occur just in the relevant region [17]. In \([\text{Cu}\{\text{ONC}(\text{CN})_2\}_2(\text{py})_2]\) according to the X-ray results the NiN\(_2\)O\(_2\) chromophore shows a \(D_3h\) symmetry and three IR active skeletal stretching modes, \(v_\text{Z}\), \(B_{1u}\), \(B_{2u}\) and \(B_{3u}\), can be expected. Three absorption bands assignable to these modes were found, the one appearing at low frequency being slightly split, very likely by crystal structure effects. In \([\text{Cu}\{\text{ONC}(\text{CN})_2\}_2(\text{py})_4]\) only long axial Cu–ONC(CN)\(_2\) bonds are present so that the corresponding stretching modes cannot be present in the investigated region but occur in the low-energy region below 100 cm\(^{-1}\) [18]. Therefore, the band at 299 cm\(^{-1}\) must be ascribed to the Cu–N(pyridine) stretch. In the case of \([\text{Cu}\{\text{ONC}(\text{CN})_2\}_2(\text{py})_2]\) short Cu–N(py) and Cu–ONC(CN)\(_2\) bonds are present in the equatorial plane. Besides \(v(\text{Cu–N(py)})\) bands similarly positioned as in the previous compound, \(v(\text{Cu–ONC(CN)\(_2\)})\) bands also appear above 300 cm\(^{-1}\).

**Ligand field spectra**

The ligand field spectra are given in Table 4. The spectrum of \([\text{Ni}\{\text{ONC}(\text{CN})_2\}_2(\text{py})_4]\) is in agreement with the approximately octahedral coordination geometry [19] determined crystallographically. The absorptions at 1.05 and ~1.75 \(\mu\text{m}^{-1}\) correspond to the \(3T_{2g} \rightarrow 3A_{2g}\) and \(3T_{1g}(F) \rightarrow 3A_{2g}\) transitions, in \(O_h\) symmetry, respectively; the \(Dq\) value is 1050 cm\(^{-1}\). Between the foregoing bands two shoulders occur. One belongs to the spin-forbidden transition into the \(1E_g\) singlet state and the second can be connected with the splitting of the octahedral \(3T_{2g}\) state by the low-symmetry component. The \(3T_{1g}(P) \rightarrow 3A_{2g}\) transition highest in energy is overlapped by an intense absorption connected with

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(\text{C}=\text{N}))</th>
<th>(\nu(\text{ONC}))</th>
<th>(\nu(\text{C}–\text{C}))</th>
<th>(\nu(\text{M-donor}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>KONC(CN)(_2)</td>
<td>2232, 2255</td>
<td>1325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Ni}{\text{ONC}(\text{CN})_2}_2(\text{py})_4])</td>
<td>2221 vs</td>
<td>1383 vs, 1353 vs</td>
<td>1275</td>
<td>1226</td>
</tr>
<tr>
<td>([\text{Co}{\text{ONC}(\text{CN})_2}_2(\text{py})_4])</td>
<td>2222 vs</td>
<td>1384 vs, 1354 m</td>
<td>1251 m, 1205 vs, 1192 sh*</td>
<td>307 m, 280 s, 254 s, 242 sh</td>
</tr>
<tr>
<td>([\text{Cu}{\text{ONC}(\text{CN})_2}_2(\text{py})_4])</td>
<td>2229 vs, 2216 vs</td>
<td>1397 vs, 1334 m</td>
<td>1248 mww, 1199 sh^1, 1189 vs</td>
<td>304 m, 295 m, 266 s</td>
</tr>
<tr>
<td>([\text{Cu}{\text{ONC}(\text{CN})_2}_2(\text{py})_2])</td>
<td>2227 vs, ~ 2230 sh</td>
<td>1394 vs, 1324 m</td>
<td>1259 mw, 1192 vs, 1186 sh^1</td>
<td>299 m, 287 sh, 266 m</td>
</tr>
<tr>
<td>([\text{Cu}{\text{ONC}(\text{CN})_2}_2(\text{py})_4])</td>
<td>1250 mw</td>
<td>1175 vs, 1156 s</td>
<td>315 m, 304 sh, 292 s, 270 m</td>
<td></td>
</tr>
</tbody>
</table>

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**Table 3. Characteristic IR data [cm\(^{-1}\)].**

**Table 4. Ligand field spectra.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\varphi_{\text{max}} [\mu\text{m}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni}{\text{ONC}(\text{CN})_2}_2(\text{py})_4])</td>
<td>1.05, ~ 1.20 sh, ~ 1.27 sh, ~ 1.75 sh</td>
</tr>
<tr>
<td>([\text{Co}{\text{ONC}(\text{CN})_2}_2(\text{py})_4])</td>
<td>0.96, ~ 2.1 sh</td>
</tr>
<tr>
<td>([\text{Cu}{\text{ONC}(\text{CN})_2}_2(\text{py})_2])</td>
<td>1.64</td>
</tr>
<tr>
<td>([\text{Cu}{\text{ONC}(\text{CN})_2}_2(\text{py})_4])</td>
<td>1.67, ~ 1.37 sh</td>
</tr>
</tbody>
</table>
charge transfer transitions. The d-d spectrum of [Co{ONC(CN)2}2(py)4] is also consistent with an octahedral central atom environment [19] and the coordination is very probably that the same as in the previous compounds. The absorptions at 0.96 and $\approx 2.1 \, \text{cm}^{-1}$ can be assigned to the $4T_{2g} \rightarrow 4T_{1g}(F)$ and $4T_{1g}(P) \rightarrow 4T_{1g}(F)$ transitions in the $O_h$ field. From these transitions values of 1000 and 786 cm$^{-1}$ follow for the $D_q$ and $B$ parameters, respectively. The $D_q$ value is very similar to that of the Ni(II) complex, the $\beta$ value of 0.81 indicates a distinct degree of covalency.

The ligand field spectra of both copper(II) complexes contain one visible band with a long tail towards the infrared region. The spectrum of [Cu{ONC(CN)2}2(py)2] shows an ill resolved shoulder on this tail. The positions and forms of these bands indicate six-coordinated pseudo-octahedral structures with four short equatorial and two long axial bonds [20]. The d-d bands comprise at least three electronic transitions in the central Cu(II) atom ($d_{xy}, d_{yz}, d_{z^2} \rightarrow d_{x^2-y^2}$); the low-energy shoulder in the spectrum of [Cu{ONC(CN)2}2(py)2] very likely belongs to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. In the case of the bis(pyridine) compound the dicyanomethanidonitrite anions exhibit a bridging function between two adjacent structural units. These bridging anions probably use their nitrile nitrogen atoms for forming long axial bonds. According to the d-d bands the tetragonal distortion in both copper(II) complexes is very similar.