NUCLEOPHILIC ADDITION IN TRANSITION METAL, PSEUDOHALIDE–4-NITROPYRAZOLE SYSTEMS

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Dedicated to Professor Jiří Klikorka on the occasion of his 70th birthday.

The possibility of nucleophilic addition of 4-nitropyrazole (4-NO_2-pz) to a pseudohalide group present in the coordination sphere of a central atom was investigated. Ten products were isolated from M(II)–X^--4-nitropyrazole systems with M = Cu, Ni or Co and X = NCO, $N(CN)_2$ or $C(CN)_3$, and investigated by infrared and electronic spectroscopy. Four of these compounds were pseudohalide complexes, two were complexes with anionic chelate ligands formed by nucleophilic addition, and the remaining products were mixtures of pseudohalide and chelate complexes. The $[Cu(NCO)_2(4\text{-}NO_2\text{-pz})_2]$ complex is rhombic-octahedral or five-coordinate, the $[Cu(NCO)_2(4\text{-}NO_2\text{-pz})]$ complex is five-coordinate. The remaining compounds possess octahedral or pseudooctahedral structures which involve pseudohalide bridging in the $[MX_2(4\text{-}NO_2\text{-pz})_2]$ type complexes, or bridging via free carbamoyl oxygens or cyanide nitrogens in the $[M(4\text{-}NO_2\text{-pz.X})_2]$ type complexes.

Reactions of nucleophilic addition have been found[1 – 14] to occur between pseudohalide ions and pyrazole type ligands in the coordination sphere of some transition metals. In these reactions the imine nitrogen of the pyrazole ring is bonded to the carbon atom of the pseudohalide anion, which is associated with the formation of new anionic chelate ligands (Fig. 1). Since the corresponding pseudohalide complexes have also been prepared from the systems studied, isomeric pairs have been so obtained; these have been referred to by us as coligand isomers[4,5].

The series of papers[1 – 9,11 – 14] has dealt with the effect of the central atom and the anionic and pyrazole ligands on the course of the above reaction. In the case of the cyanate group and the Cu(II) atom[1 – 7,14], the nucleophilic addition has been found affected by the electron density in the methylpyrazoles or halopyrazoles. With nonlinear pseudohalides such as dicyanamide and tricyanomethanide, however, this phenomenon has not been confirmed[11,12,14]; the steric effects of these ligands, which depend on their shape, seem to play a more important role in this case. The nucleophilic addition has also been observed to proceed considerably more readily in copper(II) systems[1 – 7,9,12,14] than in nickel(II) systems[8,9,12,14]. In the case of cobalt(II) (ref.[8]), no pure product with anionic chelate ligands has been as yet isolated.

In order to further examine the conditions of the nucleophilic addition, we investigated systems involving Cu(II), Ni(II) or Co(II) atoms, cyanate, dicyanamide or tricyanomethanide ligands, and 4-nitropyrazole; in the last compound, the pyrazole ring electron density is reduced considerably by the strong negative *I*-effect of the nitro group. To make the results comparable, the preparation conditions were mostly identical. Ten substances, representing pseudohalide complexes, chelate complexes and their mixtures were prepared and subjected to examination by infrared and electronic spectroscopy.

EXPERIMENTAL

Preparation of Ligands and their Metal Complexes

4-Nitropyrazole ($4\text{-}NO_2\text{-}pz$) was prepared from pyrazole by nitration as described by Buchner and Fritsch[15]. $[MX_2(4\text{-}NO_2\text{-}pz)_2]$ and $[M(4\text{-}NO_2\text{-}pz.X)_2]$ where M = Cu or Ni and X = NCO, $N(CN)_2$ or $C(CN)_3$, mixtures of compounds of these types with X^- = NCO, $C(CN)_3$, as well as $[MX_2(4\text{-}NO_2\text{-}pz)_4]$ +

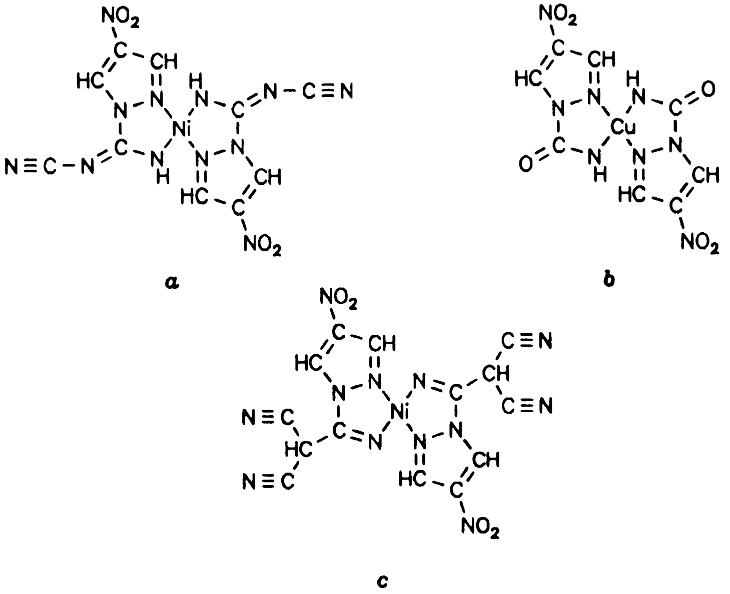

FIG. 1

Proposed structures of the products of nucleophilic additions: *a* $[Ni\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$, *b* $[Cu(4\text{-}NO_2\text{-}pz.NCO)_2]$, *c* $[Ni\{4\text{-}NO_2\text{-}pz.C(CN)_3\}_2]$

[M(4-NO_2-pz.X)$_2$] mixtures where M = Ni, Co and X = NCO, were synthetized as follows. Warm (40 °C) aqueous solution of $Cu(NO_3)_2 \cdot 6\,H_2O$, $Ni(NO_3)_2 \cdot 6\,H_2O$ or $Co(NO_3)_2 \cdot 6\,H_2O$ was mixed with warm (40 °C) aqueous solution of KNCO, $KN(CN)_2$ or $KC(CN)_3$ and with warm (40 °C) methanolic solution of 4-nitropyrazole with continuous stirring. The corresponding complex precipitated in the form of a fine crystalline material, which was collected, washed with a water–methanol mixture, and dried in a desiccator over KOH.

The solutions used included those of $Cu(NO_3)_2 \cdot 3\,H_2O$, $Ni(NO_3)_2 \cdot 6\,H_2O$ or $Co(NO_3)_2 \cdot 6\,H_2O$ (5 mmol in 5 cm^3 of water), KNCO (11 mmol in 7 cm^3 of water), $KN(CN)_2$ or $KC(CN)_3$ (11 mmol in 10 cm^3 of water), and 4-NO_2-pz (12 mmol in 10 cm^3 of methanol).

[$Cu(NCO)_2$(4-NO_2-pz)$_2$] was prepared at 5 °C from 5 mmol of $Cu(NO_3)_2 \cdot 3\,H_2O$ dissolved in 5 cm^3 of cool water, by mixing with a solution containing 11 mmol of KNCO in 6 cm^3 of cool water, followed by addition of 12 mmol of 4-NO_2-pz in 10 cm^3 of cool methanol. The compound precipitated in the form of fine crystals.

[$Cu(NCO)_2$(4-NO_2-pz)] was prepared from 5 mmol of $Cu(NO_3)_2 \cdot 3\,H_2O$ dissolved in 5 cm^3 of water by mixing with a solution of 11 mmol of KNCO in 6 cm^3 of water, followed by addition of 5.5 mmol of 4-NO_2-pz in 7 cm^3 of methanol. All solutions were used at room temperature. Fine crystals of the compound precipitated.

[Ni{$N(CN)_2$}$_2$(4-NO_2-pz)$_2$] was prepared in the same way as [Ni{4-NO_2-pz.$N(CN)_2$}$_2$] except that the solutions were used at room temperature.

Analyses

Copper, nickel and cobalt were determined chelometrically after decomposing the compounds with dilute H_2SO_4 and oxidizing the organic component with $K_2S_2O_8$. Elemental analyses were carried out on a Carlo Erba CHN-analyser. The analytical data of the compounds are summarized in Table I.

Physico-Chemical Measurements

Infrared spectra of Nujol mulls were measured over the region of 4 000 – 400 cm^{-1} on a Specord M80 spectrophotometer (Carl Zeiss, Jena) and over the region of 500 – 200 cm^{-1} on a Philips PU 9800 FTIR spectrometer. Electronic spectra were measured over the region of 3.5 – 0.5 μm^{-1} on a Beckman UV 5240 spectrometer in the diffuse reflectance mode using MgO as the diluting agent.

RESULTS AND DISCUSSION

Infrared Spectra

In the mid-IR, only those bands that are of importance with respect to the course of the nucleophilic addition were examined for the complexes studied. The metal–nitrogen stretching vibration frequencies were established in the far-IR region. Some selected infrared spectral data are given in Table II.

In all the cyanate complexes studied, the $C\equiv N$ stretching vibration bands lie near 2 180 cm^{-1}, which is considerably lower than the conventional occurrence at about 2 220 cm^{-1} (ref.[16]). This fact may be a result of the strong negative *I*-effect of the NO_2 group on the pyrazole ring, due to which the electron density in the cyanate group is shifted towards the coordinated nitrogen. The δ bending mode (not listed in Table II) appears nearly above 600 cm^{-1} for all of the cyanate complexes. This band is not split or is split only weakly; the $[Cu(NCO)_2 . (4\text{-}NO_2\text{-}pz)]$ complex is an exception, exhibiting four weak to medium-intensity bands at 665, 638, 614 and 603 cm^{-1} (the last-mentioned band cannot be discriminated with certainty from the 4-NO$_2$-pz band). This splitting of the bending vibration is indicative of the bridging function of the NCO group where the nitrogen atom acts as a bidentate donor[16].

The compounds $[Cu\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$ and $[Ni\{N(CN)_2\}_2 . (4\text{-}NO_2\text{-}pz)_2]$ exhibit $C\equiv N$ stretching frequencies which indicate bidentate bridging bonding of the pseudohalide groups through the nitrogen atom[17 – 19].

In addition to the $\nu(C\equiv N)$ bands at usual frequencies, the spectra of the compounds $[Cu\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$ and $[Ni\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$ also exhibit new, very strong

TABLE I
Analytical and other characteristic data of the complexes prepared

Compound	Colour	Calculated/Found			
		% C	% H	% N	% M
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)_2]$	blue	25.71 25.13	1.62 1.71	25.69 25.28	17.00 16.78
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)]$	navy blue	23.04 22.43	1.16 1.27	26.87 26.12	24.38 24.25
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)_2]$ + $[Cu(4\text{-}NO_2\text{-}pz.NCO)_2]$	dark blue	25.71 24.98	1.62 1.79	25.69 25.17	17.00 16.63
$[Cu\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$	grey-blue	28.48 27.69	1.43 1.51	39.85 39.21	15.06 14.78
$[Cu\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$	yellow-green	35.79 35.03	1.29 1.14	35.78 34.91	13.52 13.81
$[Ni(NCO)_2(4\text{-}NO_2\text{-}pz)_4]$ + $[Ni(4\text{-}NO_2\text{-}pz.NCO)_2]$	rose-brown	27.41 26.87	1.88 1.88	31.96 31.31	12.22 11.87
$[Ni\{N(CN)_2\}_2(4\text{-}NO_2\text{-}pz)_2]$	light blue	28.80 28.44	1.44 1.56	40.31 39.72	14.00 13.79
$[Ni\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$	pale blue-grey	28.80 28.51	1.44 1.53	40.31 39.88	14.00 14.11
$[Ni\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$ + $[Ni\{4\text{-}NO_2\text{-}pz.C(CN)_3\}_2]$	light violet	36.53 36.02	1.31 1.45	36.52 35.96	12.76 12.43
$[Co(NCO)_2(4\text{-}NO_2\text{-}pz)_4]$ + $[Co(4\text{-}NO_2\text{-}pz.NCO)_2]$	orange-brown	27.41 26.53	1.88 1.97	31.96 30.58	12.22 12.47

TABLE II
Characteristic infrared frequencies, cm^{-1}, of the compounds prepared[a]

Compound	ν(C≡N)	ν(C=O) or ν(C=N)	ν(M–N)
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)_2]$	2 183vs		350m 297ms 269m
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)]$	2 188vs		382w 345mw 293m 265mw
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)_2]$ + $[Cu(4\text{-}NO_2\text{-}pz.NCO)_2]$	2 183vs	1 738vs 1 706vs	365w 345mw 294m 265mw
$[Cu\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$	2 162vs	1 620vs	348ms 290sh 273s
$[Cu\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$	2 262vs 2 210sh 2 192vs		348m 298s 290sh 272m 263sh
$[Ni(NCO)_2(4\text{-}NO_2\text{-}pz)_4]$ + $[Ni(4\text{-}NO_2\text{-}pz.NCO)_2]$	2 180ms	1 658sh 1 610ms	326m 299ms
$[Ni\{N(CN)_2\}_2(4\text{-}NO_2\text{-}pz)_2]$	2 257ms 2 190vs		335vw 293s 247s
$[Ni\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$	2 185vs	1 745vs 1 710m 1 620m	294ms 285ms 247s
$[Ni\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$ + $[Ni\{4\text{-}NO_2\text{-}pz.C(CN)_3\}_2]$	2 259m 2 210ms 2 187vs	1 630m	288w 256s
$[Co(NCO)_2(4\text{-}NO_2\text{-}pz)_4]$ + $[Co(4\text{-}NO_2\text{-}pz.NCO)_2]$	2 180s	1 705s 1 666s	377b,sh

[a] s strong, m medium, w weak, v very, sh shoulder, b broad.

bands within the range of 1 745 – 1 620 cm^{-1}, which are in all likelihood associated with the vibration of the C=N group as a constituent of a new anionic chelate ligand[9 – 12]. We suggest that this new ligand arises from nucleophilic addition of the pyrazole ring imine nitrogen to the carbon of the cyanide group. This reaction in the coordination sphere of the metal atom leads to the closing of the five-membered chelate ring (Fig. 1*a*). The remaining cyanide group in the chain is responsible for the stretching mode as usually found for the $C\equiv N$ bond. In the case of the Cu(II) complex, the band at 1 258 cm^{-1} belongs to the C–N bond[9,12]; in the spectrum of the Ni(II) complex this band is overlapped by the ligand bands.

The infrared spectra of the products isolated from the cyanate systems involve strong bands of two kinds, viz. at approximately 2 180 cm^{-1} and roughly within the 1 740 – 1 610 cm^{-1} range. Whereas the former bands correspond to the cyanate $\nu(C\equiv N)$ vibration[16], the latter bands can be assigned to the $\nu(C=O)$ vibration of the anionic chelate ligands formed by nucleophilic addition of the pyrazole imine nitrogen to the carbon of the cyanate group[1 – 5]. From this fact we conclude that the respective compounds consist of two different species: cyanate complexes and 4-nitro-1-carbamoylpyrazolate complexes (Fig. 1*b*). The situation with the product isolated from the system containing Ni(II) and tricyanomethanide is similar. This product displays strong $\nu(C\equiv N)$ bands belonging to the tricyanomethanide complex, which resemble closely the bands observed in the spectrum of $[Cu\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$. In addition, a medium intensity band which can be attributed to the $\nu(C=N)$ stretching vibration appears at 1 630 cm^{-1}. This band suggests the presence of some amount of a species with anionic chelate ligands formed by nucleophilic addition analogous to the case of dicyanamide (Fig. 1*c*).

For the metal–nitrogen stretching modes, a variable number of bands (one to five) were identified within the relatively broad region of approximately 380 – 250 cm^{-1}. In the spectra of the cyanato–copper(II) complexes, the band observed at 380 – 345 cm^{-1} can be attributed to the Cu–NCO stretching mode[16]; for $[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)]$ this band is split. The spectra of the coligand isomers $[Ni\{N(CN)_2\}_2(4\text{-}NO_2\text{-}pz)_2]$ and $[Ni\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$ differ substantially in the position of the highest-frequency band, which is well above 300 cm^{-1} in the spectrum of the dicyanamide complex. This fact may be interpreted so (refs[20,21]) that the dicyanamide ligand forms bridges which involve both the cyanide and amide nitrogens. However, this band is very weak and therefore caution must be exercised when considering this suggestion. As to the remaining systems, it is rather difficult to discriminate the $\nu(M\text{–}N)$ stretching bands associated with the chemically different nitrogen atoms.

Electronic Spectra

The electronic ligand field band data of the compounds under study are listed in Table III. The electronic spectra of the copper(II) complexes show broad ligand field bands with maxima within the region of 1.5 – 1.65 μm^{-1} and mostly also shoulders on the lower- or higher-frequency side. Such spectra are typical for distorted six- or five-coordinate arrangement of donor atoms around the Cu(II) atom[22].

The compound $[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)_2]$ is, in view of the higher-frequency shoulder, apparently rhombic-octahedral or five-coordinate (tetragonal pyramid[23]). The central Cu(II) atom is trans-coordinated in a nearly square-planar geometry by the cyanate and tertiary pyrazole nitrogens, and these structure units are completed to six- or five-coordinate forms by cyanate oxygens from the adjacent units. Analogous structures have also been suggested for other $[Cu(NCO)_2L_2]$ compounds based on their spectral patterns[2,14,24].

The cyanato-copper(II) complex involving one $4\text{-}NO_2\text{-}pz$ molecule displays the $d \leftarrow d$ band in a similar position, which also suggests five-coordination in this case; however, infrared spectra give evidence of the occurrence in this compound of bidentate cyanate nitrogens[16], through which the basic structure units are linked into polymeric chains. Such polymeric chain structure has been revealed for $[Cu(NCO)_2(2,4\text{-lutidine})]$ by single-crystal X-ray analysis[25].

In the spectrum of a mixture of the cyanate complex with the carbamoylpyrazolate complex, the peak of the broad $d \leftarrow d$ band is roughly 0.1 μm^{-1} shifted to higher wavenumbers with respect to the above compound. This band involves two maxima for the two isomeric species; the observed shift is due to the six-coordinate $[Cu(4\text{-}NO_2\text{-}pz.NCO)_2]$. In this complex, the square-planar chelates are completed by free carbamoyl oxygens to the tetragonal bipyramidal configuration.

The structure of $[Cu\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$ is pseudooctahedral and the free cyanide nitrogens combine the square-planar chelates into a six-coordinate species. The diffe-

TABLE III
Electronic spectral data of the compounds prepared

Compound	$\tilde{\nu}_{max}$, μm^{-1} [a]
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)_2]$	1.52 ≈ 1.78sh
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)]$	≈ 1.39sh 1.54
$[Cu(NCO)_2(4\text{-}NO_2\text{-}pz)_2]$ + $[Cu(4\text{-}NO_2\text{-}pz.NCO)_2]$	1.61b
$[Cu\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$	1.65
$[Cu\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$	≈ 1.20sh 1.55
$[Ni(NCO)_2(4\text{-}NO_2\text{-}pz)_4]$ + $[Ni(4\text{-}NO_2\text{-}pz.NCO)_2]$	1.08 ≈ 1.32sh 1.83 ≈ 2.70sh
$[Ni\{N(CN)_2\}_2(4\text{-}NO_2\text{-}pz)_2]$	1.04 ≈ 1.35sh 1.72b
$[Ni\{4\text{-}NO_2\text{-}pz.N(CN)_2\}_2]$	1.06 ≈ 1.19sh ≈ 1.35sh 1.80b
$[Ni\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2]$ + $[Ni\{4\text{-}NO_2\text{-}pz.C(CN)_3\}_2]$	1.09 ≈ 1.38sh 1.77 ≈ 2.72sh
$[Co(NCO)_2(4\text{-}NO_2\text{-}pz)_4]$ + $[Co(4\text{-}NO_2\text{-}pz.NCO)_2]$	0.66 – 0.96 ≈ 2.15sh

[a] For abbreviations see Table II footnote; [b] overlapped by an intense UV absorption.

rence between the wavenumbers of the maximum and the shoulder indicates that the tricyanomethanido copper(II) complex is pseudooctahedral[22], formed by structure units which are analogous to those in the cyanate complex; the bridging tricyanomethanide groups, however, participate in completing the coordination.

All the nickel(II) complexes under study have similar electronic spectra which exhibit the spin-allowed $d \leftarrow d$ bands at about 1.07 and 1.77 μm^{-1} and shoulders at about 2.70 μm^{-1}. The latter absorption is in some cases overlapped by a very intense UV band. These spectra unambiguously indicate[26] an octahedral environment of the Ni(II) atom in the complexes without apparent distortion. The respective $d \leftarrow d$ absorptions in the order of increasing wavenumbers are assigned to the transitions ${}^3T_{2g} \leftarrow {}^3A_{2g}$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$, and ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$. The 10 Dq values, which are equal to the energies of the ${}^3T_{2g} \leftarrow {}^3A_{2g}$ transition, are very close to one another, hence, the ligand field strength is very similar in all the substances. This fact is noteworthy because the compounds differ in the number of 4-NO_2-pz molecules involved, in the functionality of the pseudohalides and even in the kinds of the anionic ligands.

The spectrum of the single Co(II) substance which has a mixed character indicates[27] an octahedral stereochemistry of the coordination sphere. This is apparently analogous to the case of the $[Ni(NCO)_2(pz)_4]$ + $[Ni(4\text{-}NO_2\text{-}pz.NCO)_2]$ mixture. In one of these components the central atom is surrounded by tertiary nitrogens from 4-nitropyrazole in a square-planar fashion, while the cyanate nitrogens are trans-coordinated in axial positions. In the second component the chelates are planar, bonded by cyanide nitrogens from adjacent structural units, which is associated with the formation of octahedral systems.

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