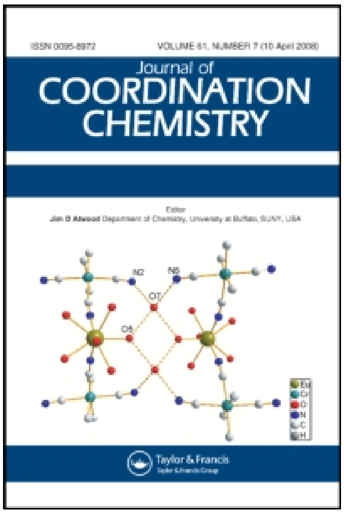

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A NOVEL TYPE OF NUCLEOPHILIC ADDITION IN THE CENTRAL ATOM COORDINATION SPHERE; REACTION BETWEEN A NON-LINEAR PSEUDOHALIDE ANION AND A PYRAZOLE-TYPE BASE

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NOTE

A NOVEL TYPE OF NUCLEOPHILIC ADDITION IN THE CENTRAL ATOM COORDINATION SPHERE; REACTION BETWEEN A NON-LINEAR PSEUDOHALIDE ANION AND A PYRAZOLE-TYPE BASE

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In recent years nucleophilic addition between the cyanate group and pyrazole or its methyl-derivative in the Cu(II) coordination sphere has been thoroughly studied.[1–4] From the systems Cu(II)-NCO^--pyrazole-type ligand as well as the compounds in which a nucleophilic reaction was realized, isomeric cyanato complexes were also separated ("coligand" isomerism).[3] Earlier investigations showed that the non-linear pseudohalide anions dicyanamide, $N(CN)_2^-$, and tricyanmethanide, $C(CN)_3^-$, closely resemble the cyanate ligand.[5] Based on the pseudochalcogen character of NCN and $C(CN)_2$ groups,[6] these pseudohalides may be classified as pseudochalcogenates.[7] We supposed therefore that in systems with these non-linear pseudohalides nucleophilic addition also could take place and the occurence of further coligand isomers could be expected.

From the systems M(II)-X^--L, where M = Cu, Ni; X = $N(CN)_2$, $C(CN)_3$; L = pyrazole (pz), benzopyrazole (indazole, inz), four pairs of isomeric compounds of the type MX_2L_2 and $M(L.X)_2$ were isolated as crystalline powders.[8] The analytical results of C, H, N and metal determinations were satisfactory. As we did not succeed in preparing single crystals suitable for X-ray crystallographic studies, we characterized these compounds structurally by applying indirect methods.[8] In this communication, the IR spectral data are preliminarily reported (Table I).

Generally, the IR features of the compounds of both types are so much dissimilar that the structures of the attached ligands must be considerably different. The MX_2L_2 complexes exhibit in the range of *ca* 2250–2140 cm^{-1} two or three intense bands, which are doubtless due to the C≡N vibration.[5] From the number and position of these bands it may be supposed that in the MX_2L_2 complexes the dicyanamide or tricyanmethanide ligands are involved in bidentate bridging functions, using nitrogens of two cyanide groups.

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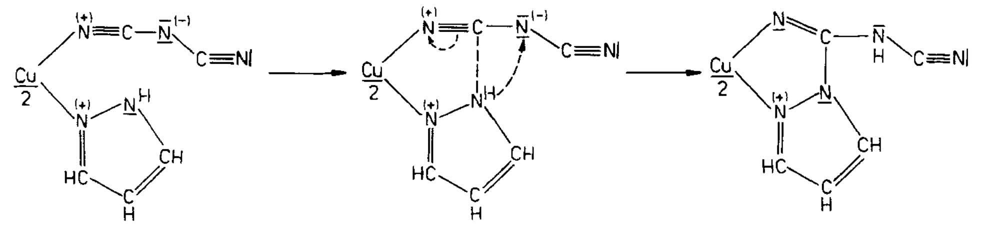
TABLE I
Characteristic infrared bands (cm^{-1}) of MX_2L_2 and $M(L\cdot X)_2$ complexes.

Compound	$\nu(C\equiv N)$	$\nu(C=N)$	$\nu_{as}(NCN)$	$\nu(C-N)$
$Cu\{N(CN)_2\}_2(pz)_2$	2240s, 2182vs			
$Cu\{C(CN)_3\}_2(pz)_2$	2242s, 2185vs			
$Cu\{N(CN)_2\}_2(inz)_2$	2244s, 2175vs			
$Ni\{N(CN)_2\}_2(pz)_2$	2248s, 2179vs, 2139vs			
$Cu\{pz\cdot NCNCN\}_2$	2164vs	1625vs	1415vs	1231s
$Cu\{pz\cdot NCC(CN)_2\}_2$	2203s, 2181vs	1575vs	1421s[a]	1209m
$Cu\{(inz\cdot NCNCN\}_2$	2230sh, 2170vs	1627sh, 1620vs	1415vs	1211w
$Ni\{pz\cdot NCNCN\}_2$	2251ms, 2180vs, 2147vs	1597vs	1441vs	1207m

[a] Assigned to ν_{as} (NCC).

With the $M(L\cdot X)_2$ complexes the $C\equiv N$ stretching bands in the region mentioned are also present, but other new, very strong bands appear between 1625–1575 cm^{-1}, which may be assigned only to the $C=N$ stretching vibration.[9] From this fact and by analogy to the compounds obtained from similar systems with the cyanate group[1–4] we conclude that these compounds are coligand isomers of the MX_2L_2 complexes, arising by nucleophilic addition of one cyanide group to the imine nitrogen of the pyrazole ring. Thus, new anionic chelate ligands in the metal coordination sphere are formed, as for $Cu\{pz\cdot NCNCN\}_2$, shown in Scheme 1 (only equatorial bonds are marked). Instead of the $-NH-C\equiv N$ chain in the case of $Cu\{pz\cdot NCC(CN)_2\}_2$ that of $-CH=(C\equiv N)_2$ is supposed.

SCHEME 1



The weak to strong bands above 1200 cm^{-1} are attributable to the C–N stretching mode in these ligands, as in the case of similar carbamoylpyrazolato compounds.[1–4] The assignment of the bands in the region of ≈1440–1415 cm^{-1}, missing in the spectra of the MX_2L_2 complexes, is not straightforward, but most reasonably they are thought to correspond to asymmetric NCN or NCC stretches.

It should be emphasized that the results obtained demonstrate a fundamental parallel between the reactivity of the pseudohalide NCY^- [$Y = O$, NCN, $C(CN)_2$] bonded in the metal coordination sphere towards the pyrazole-type base.

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