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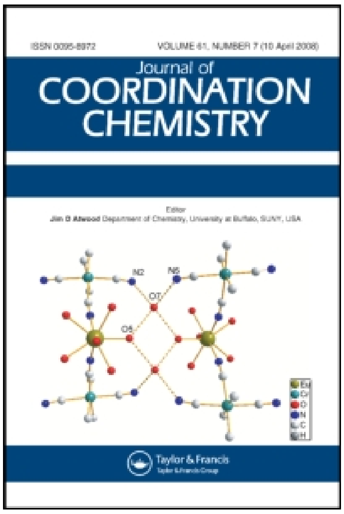

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Tricyanomethanide and Dicyanamide Complexes of Cu(II), Ni(II), Co(II), Their Structures and Properties

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Review

TRICYANOMETHANIDE AND DICYANAMIDE COMPLEXES OF Cu(II), Ni(II), Co(II), THEIR STRUCTURES AND PROPERTIES

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This review summarizes data for all known tricyanomethanide and dicyanamide compounds of copper(II), nickel(II) and cobalt(II). The possible bonding modes of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions and their influence on infrared spectra are demonstrated. Preparative methods are briefly described and structural data for crystallographically characterized compounds are given. Data for electronic and ESR spectra, magnetic susceptibilities, vibrational and ESCA spectra are reviewed and consequences following from these techniques for structural characteristics are discussed. The most striking features of the behaviour of both pseudohalide ligands are their polydentate character and ability for bridging. This ability is revealed by many physical properties, especially by the temperature dependence of magnetic susceptibilities, in which exchange interaction through pseudohalide bridges is manifested. Reactivity of $C(CN)_3$ and $N(CN)_2$ groups in the coordination sphere of Cu(II) and Ni(II) is mentioned.

Keywords: Tricyanomethanide; dicyanamide; copper(II); nickel(II); cobalt(II); structures

CONTENTS

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[*] Corresponding author.

0 ABBREVIATIONS

ampy	aminopyridine
BEDT-TTF	3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene
biz	benzimidazole

bpy	2,2′-bipyridine
cha	cyclohexylamine
dmpz	3,5-dimethylpyrazole
DMSO	dimethylsulfoxide
ET = BEDZ-TTF	bis(ethylenedithio)tetrathiafulvalene
en	ethylenediamine
etbiz	ethylbenzimidazole
etpy	ethylpyridine
form	*N*,*N*′-di-*p*-toxylformamidinate
HMPA	hexamethylphosphoramide
hmt	hexamethylentetramine
inz	indazole (benzopyrazole)
i-quin	isoquinoline
iz	imidazole
lut	lutidine (dimethylpyridine)
mcoe	methyl-2-cyano-2-(hydroximino)ethandiaminate
Me	methyl
mebiz	methylbenzimidazole
meiz	methylimidazole
mici	dimethylimidodicarbonimidate
nipy	nitropyridine
OMNA	*N*-oxymethylnicotinamide
Ph	phenyl
phz	phenazine
PCy_3	tricyclohexylphosphane
phen	1,10-phenantroline
pic	picoline (methylpyridine)
PPh_3	triphenylphosphane
py	pyridine
pyz	pyrazine
pz	pyrazole
quin	quinoline
tmpz	3,4,5-trimethylpyrazole
TPP	5,10,15,20-tetraphenylporphinate

1 INTRODUCTION

Tricyanomethanide ion was discovered in 1896 by Schmidtmann[1] who synthesized $K[C(CN)_3]$. Dicyanamide ion $[N(CN)_2]^-$ was first time described in

1922 by Madelung and Kern.[2] In agreement with the pseudohalide concept[3-5] new results show that $[NCO]^-$, $[C(CN)_3]^-$ and $[N(CN)_2]^-$ are very similar species. According to the pseudochalcogen concept, which was decisively developed by Köhler,[6-12] the fragments NCN and $C(CN)_2$ can be discussed as pseudochalcogens. Therefore, the ions $[NCY]^-$ ($Y = NCN$, $C(CN)_2$) appear as pseudochalcogeno-cyanates and behave so.

As a feature of this group of ions it can be estimated that in the series $[NCO]^-$, $[C(CN)_3]^-$, $[N(CN)_2]^-$ the tendency to form bridges drastically increases as a result of the character and number of donor atoms. These bridges are revealed in magnetic properties which are controlled by exchange interactions. Observed interactions are ferromagnetic or antiferromagnetic in character[13-16] and both types of interactions simultaneously operate.[17]

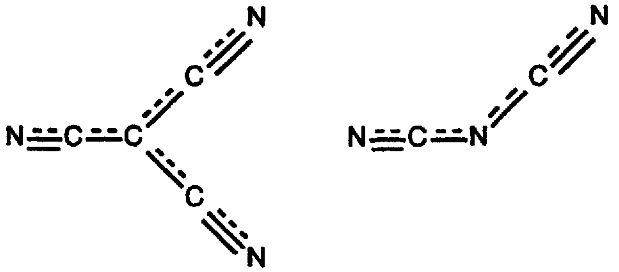
Similar to the $[NCO]^-$ ion, $[N(CN)_2]^-$ and $[C(CN)_3]^-$ ions exhibit a reactivity in the coordination sphere of some metals.[18] In systems of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ with pyrazole ligands in the coordination sphere of Cu(II), Ni(II), Pd(II) and Pt(II) a nucleophilic addition takes place and new anionic chelate ligands of carbamoylpyrazolate type are formed.[19-22] The dicyanamide group seems to be more reactive and in the Cu(II) coordination sphere it enters with methanol into a specific reaction forming a six-membered anionic chelate ligand, dimethylimidodicarbonimidate.[23,24]

The systematic study of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ as ligands in coordination chemistry began only 30 years ago. Köhler and coworkers published a notable series of basic papers on compounds of transition and some main group elements with these pseudohalides.[6] In this paper we introduce the ligand properties of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ and report complexes of Cu(II), Ni(II) and Co(II) with special regard to their structural peculiarities in pseudohalide systems especially in comparison with cyanate complexes.

2 STRUCTURES OF $[C(CN)_3]^-$ AND $[N(CN)_2]^-$ IONS AND THEIR BONDING MODES

2.1 Structural Properties of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ Ions

Geometry optimizations by use of *ab initio* methods for the $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions were performed.[25] X-ray analyses of potassium and sodium tricyanomethanide reveal that the $[C(CN)_3]^-$ ion has a strictly planar structure.[26,27] In $Na[C(CN)_3]$[27] the C–C bond length amounts to 1.408(3) Å and C–N varies between 1.145(3) and 1.164(2) Å. The C–C–C bonding angles



SCHEME 1 Approximate electronic structures of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions.

are 119.2(2)°, 120.1(2)° and 120.7(2)°, near to 120° expected for a central carbon atom of sp^2 hybridization type.

In the case of $[N(CN)_2]^-$ X-ray analysis ascertained a bent structure[28] which was supposed on the basis of vibrational spectra.[29,30] For $Cs[N(CN)_2]$[28] the following geometric parameters were found: C–N = 1.26(2) and 1.13(2) Å, N–C = 1.31(2) and 1.18(2) Å. The C–N–C and N–C–N angles amount to 124(2)° and 172(2)°, respectively. The last parameter indicates a distinct deviation from the linearity.

In agreement with the given structural data, the bonding relations in $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions can be described with the electronic structures as shown in Scheme 1. In the sense of the MO theory a marked participation of strongly delocalized π-bonds can be expected.

Extended Hückel calculations[31,32] showed that in $[C(CN)_3]^-$ the ionic charge is concentrated on the terminal nitrogen atoms. In contrast to the terminal atoms the central carbon atom is only slightly negatively charged. For $[N(CN)_2]^-$ similar relations can be assumed. In comparison to the amide nitrogen atom the cyanonitrogen atoms are characterized by somewhat higher charge density. It is necessary to note that as a consequence of the number of donating atoms the charge density on the cyanonitrogens of both the pseudohalides is rather different. Generally, these species are less basic than $[NCO]^-$.

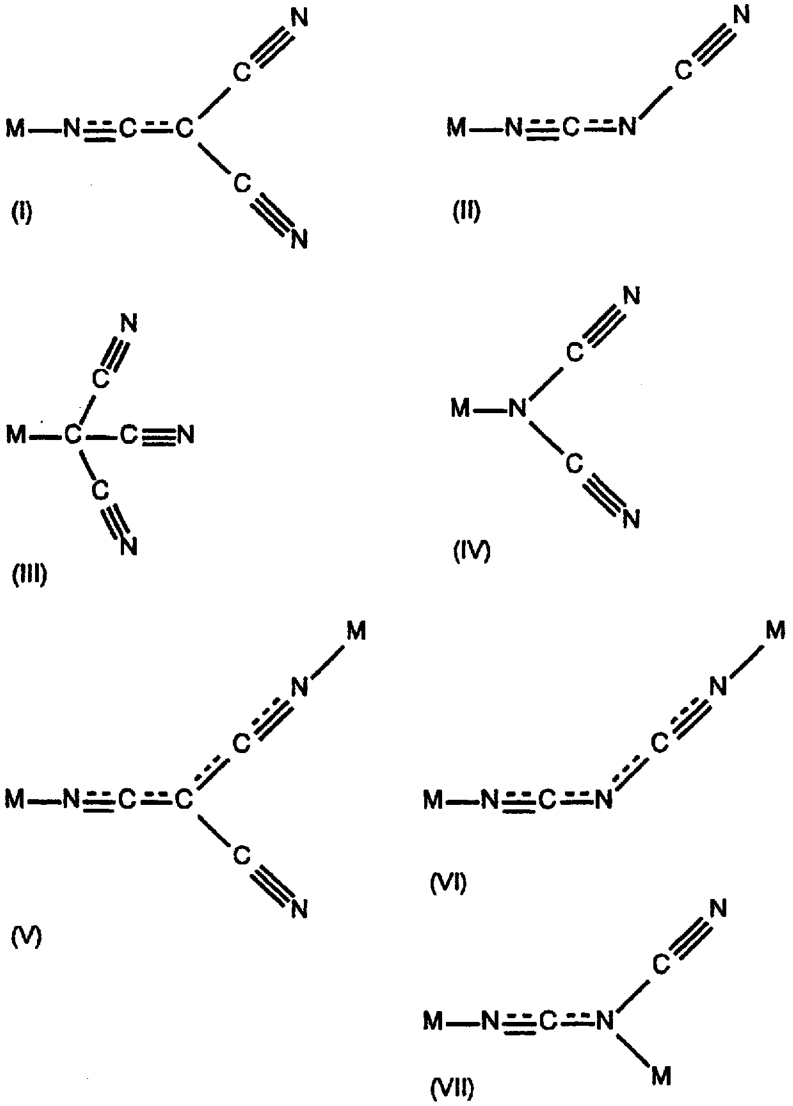
IR and Raman spectra of $[C(CN)_3]^-$ were interpreted on the basis of C_{3h} symmetry and those of $[N(CN)_2]^-$ on the basis of C_{2v} symmetry.[32] The most important vibrational frequencies are given by Köhler.[6]

2.2 Bonding Modes of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ Ions and IR Spectroscopy

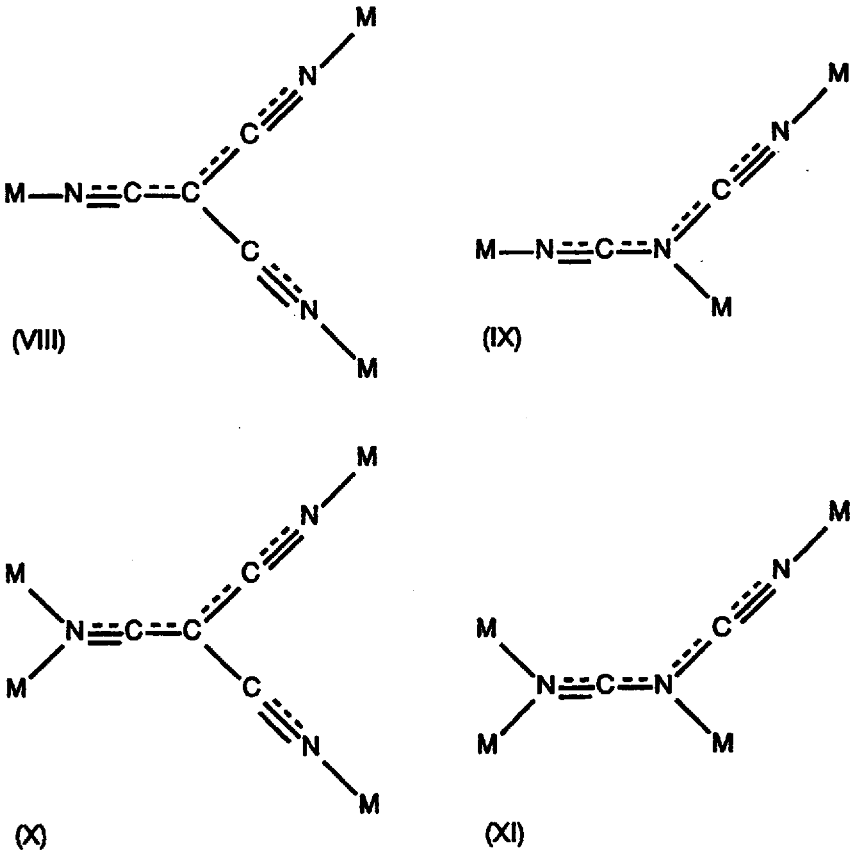
In contrast to their low basicity, $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions are able to form strong coordination bonds. The following bonding modes are possible

(Scheme 2): through the CN nitrogen (I, II), through the central carbon atom (III), through amide nitrogen (IV) or in a bridging function with participation of two, three or four donor atoms (V–XI).

The arrangement of M–N–C can be linear or bent; this can be decided only on the basis of X-ray analysis. As a result of the high electron density



SCHEME 2 (I)–(VII)



SCHEME 2 (VIII)–(XI)

SCHEME 2 Possible bonding modes of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions as ligands.

on the terminal N-atoms coordination through these donors is much more probable than other possibilities. Coordination *via* the methanide carbon (III) or the amide nitrogen (IV) is rather improbable and up to now no crystallographic evidence for it exists. The coordination type (III) was supposed only in presence of markedly soft central atoms or in covalent compounds.[6] In these species the methanide atom is sp^3 hybridized with tetrahedral geometry. In the anionic complex $[Pd\{N(CN)_2\}_4]^{2-}$ as well as in neutral complexes of the type $[M\{N(CN)_2\}_2L_2]$ ($M = Pd(II), Pt(II)$)[33,34] coordination of $N(CN)_2$ through the amide nitrogen is assumed on the basis of IR data.

In view of strong π-electron delocalization, all cyanoN-atoms in $C(CN)_3$ and $N(CN)_2$ present the same ability for coordination. Unlike cyanate these ligands have a particular tendency to bridging as bi- or tridentate ligands (V–IX).[31,35–50] The maximum denticity is four as in the case of $Me_2TlC(CN)_3$ and $Me_2TlN(CN)_2$.[51]

The coordination modes of $C(CN)_3$ and $N(CN)_2$ are frequently determined by means of vibrational spectroscopy.[6–8] For this purpose the $\nu(CN)$ vibration is of basic importance. Spectra of the free ions show strong $\nu(CN)$ bands at $2176\,cm^{-1}$ for $[C(CN)_3]^-$ in the potassium salt and 2232 as well as $2179\,cm^{-1}$ for $[N(CN)_2]^-$ in the sodium salt.[32,40] While for the NCO ligand the $\nu(CN)$ vibration, more exactly $\nu_{as}(NCO)$, does not allow any statement on the coordination mode, the $\nu(CN)$ vibration of $C(CN)_3$ and $N(CN)_2$ is often diagnostic for determination of bonding type.

When $C(CN)_3$ is a unidentate coordinated through one terminal N-atom (I), one can expect three absorptions $\nu(CN)$, $2A_1$ and B_2. In the case of arrangement (III) the symmetry is C_{3v} which results in two frequencies A_1 and E. In the IR spectra of tricyanomethanide complexes with *N*-coordinated $C(CN)_3$ two or three $\nu(CN)$ bands around 2230 and $2175\,cm^{-1}$ are frequently observed. In the case of C-coordination two $\nu(CN)$ bands should appear in same range. Distinguishing both coordination modes is impossible by means of IR spectroscopy. One can unequivocally determine the bonding relations by means of ^{14}N NMR spectroscopy. In the case of unidentate coordination of $N(CN)_2$ through cyanonitrogen (II) as a rule two $\nu(CN)$ bands appear in the ranges 2235–2220 and $2175–2160\,cm^{-1}$. Coordination through amide N-atom (IV) should cause a shift of the $\nu(CN)$ vibration to higher frequencies.

Higher functionality of $C(CN)_3$ and $N(CN)_2$ results in a higher CN bonding order and the $\nu(CN)$ vibrations are shifted to higher frequencies. Compounds with bidentate $C(CN)_3$ (V) exhibit $\nu(CN)$ bands within the ranges 2250–2240 and $2205–2185\,cm^{-1}$, with bidentate $N(CN)_2$ (VI, VII) within the ranges 2250–2235 and $2200–2190\,cm^{-1}$. Complexes with tridentate $C(CN)_3$ (VIII) show $\nu(CN)$ absorptions between 2270–2250 and $2220–2200\,cm^{-1}$, with tridentate $N(CN)_2$ (IX) 2280–2260 and $2220–2210\,cm^{-1}$. In Table I $\nu(CN)$ frequencies of some selected tricyanomethanide and dicyanamide complexes with different bonding modes of $C(CN)_3$ and $N(CN)_2$ are given. We remark that the $\nu(CN)$ band does not allow one to distinguish between coordination types (VI) and (VII).

The frequencies of the other vibrations, for instance $\nu(C–C)$ in $[C(CN)_3]^-$ or $\nu_{as}(N–C)$ in $[N(CN)_2]^-$ are not significantly influenced by the coordination type. For dicyanamide complexes a strong band around $2280\,cm^{-1}$ is typical, assigned to a combined vibration $\nu_s + \nu_{as}(C–N)$.[6]

TABLE I Frequencies of CN stretching vibrations for tricyanomethanide and dicyanamide compounds with various bonding modes

Compound	$\nu(CN)$ (cm^{-1})	*Bonding mode*	*Ref.*
$[Ni\{C(CN)_3\}_2(py)_4]$	2230, 2175	Monodentate	37
trans-$[PtH\{C(CN)_3\}(Ph_3P)_2]$	2227, 2178	Monodentate (III)[a]	52
$[Ph_4P]_2[Co\{N(CN)_2\}_2(NCS)_2]$	2230, 2168, 2070[b]	Monodentate (II)	53
$[Ph_4P]_2[Pd\{N(CN)_2\}_4]$	2255, 2185	Monodentate (IV)	33
$[Ni\{C(CN)_3\}_2(py)_2]$	2252, 2203	Bidentate	35
$[Co\{C(CN)_3\}_2(i\text{-quin})_2]$	2248,2195	Bidentate	39
$[Co\{N(CN)_2\}_2(2,4\text{-lut})_2]$	2246, 2183	Bidentate	39
$[Cu\{N(CN)_2\}_2(4\text{-pic})_2]$	2250, 2185,	Bidentate (VI)	44
$[Cu\{N(CN)_2\}_2(2\text{-etpy})_2]$	2255, 2190	Bidentate (VII)[c]	44
$[Ni\{C(CN)_3\}_2]$	2268, 2225, 2218, 2170	Tridentate	31
$[Fe\{N(CN)_2\}_2]$	2266, 2208	Tridentate	40

[a] According to ^{14}N NMR and ^1H NMR measurements. [b] The $\nu(CN)$ vibration of the NCS ligand. [c] According to the far IR spectrum.

Attempts were made[40] to distinguish the dicyanamide bonding mode on M–N stretching vibrations in the far IR region. As the M–N(nitrile) and M–N(amide) bond strengths differ, the corresponding stretching modes may be expected at different frequencies, ν(M–N(amide)) at higher frequencies than ν(M–N(nitrile)).

3 SURVEY OF PREPARED COMPOUNDS AND SYNTHETIC ROUTES

The synthetized tricyanomethanide and dicyanamide complexes of Cu(II), Ni(II) and Co(II) together with the data of ν(CN) frequencies, the wavenumbers of the ligand field band maxima, ν_{max}, of solid samples and effective magnetic moments at room temperature, μ_{eff}, are listed in Table II.

3.1 Synthesis of Tricyanomethanide and Dicyanamide Compounds MX_2; M = Cu, Ni, Co

(i) Exchange of anions by reaction of metal halides MY_2 with potassium tricyanomethanide or dicyanamide in water or absolute ethanol.

(ii) Removing of pyridine by thermal decomposition of pyridine complexes $[MX_2(py)_2]$.

3.2 Synthesis of Compounds with Complex Dicyanamide Anions

(i) The salts $M[N(CN)_2]$ (M = Me_4N, Ph_4P, Ph_4As, Ph_3MeAs) are dissolved in absolute ethanol and treated with an ethanol solution of MX_2 and alkaline salt of dicyanamide.

TABLE II Basic data for tricyanomethanido and dicyanamido complexes of Cu(II), Ni(II) and Co(II)

Compound	$\nu(CN)$ (cm^{-1})	ν_{max} (μm)	$\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$	*Ref.*
$\mathrm{[Cu\{C(CN)_3\}_2]}$	2275, 2218sh, 2210	1.39	1.86	31
$\mathrm{[Ni\{C(CN)_3\}_2]}$	[a]	0.97, 1.67, 2.55	2.86	31
$\mathrm{[Co\{C(CN)_3\}_2]}$	2268sh, 2220sh, 2208, 2160sh	0.96, 2.00, 2.13	4.79	31
$\mathrm{[Cu\{N(CN)_2\}_2]}$	2225sh, 2204		1.85	13,40
$\mathrm{[Cu, Zn\{N(CN)_2\}_2]}$		~1.10		
$\mathrm{[Ni\{N(CN)_2\}_2]}$	2260sh, 2210	0.97, 1.60, 2.614	3.18	13,40
α-$\mathrm{[Co\{N(CN)_2\}_2]}$	2250, 2210	1.93	4.98	13,40
β-$\mathrm{[Co\{N(CN)_2\}_2]}$	2275, 2192	1.66	4.60	14,40
$\mathrm{[Co, Zn\{N(CN)_2\}_2]}$		1.675		40
$\mathrm{[Ph_4As]_2[Cu\{N(CN)_2\}_4]}$	~2230, ~2170	1.297 1.23[b]		41
$\mathrm{[Me_4N]_2[Cu\{N(CN)_2\}_4]}$	~2260, ~2200	1.35		
$\mathrm{[Ph_4P][Ni\{N(CN)_2\}_3]}$	2253, 2197sh, 2184, 2165sh		3.22	40,43
$\mathrm{[Ph_4As][Ni\{N(CN)_2\}_3]}$	2250, 2185	3.17		43
$\mathrm{K[Ni_2\{N(CN)_2\}_5]}$	2280, 2212, 2183			43
$\mathrm{[MePh_3As]_2[Co\{N(CN)_2\}_3]}$	2259, 2246, 2200, 2170	5.01		42
$\mathrm{[MePh_3As]_2[Co\{N(CN)_2\}_4]}$	2257, 2243, 2195, 2170, 2233, 2185[b]	~0.70sh, 0.77, ~0.86sh, ~1.63sh, 1.65[b]	4.92	42
$\mathrm{K_2[Co\{N(CN)_2\}_4]}$		~1.61sh, 1.64[b]		42
$\mathrm{[Ph_4P]_2[Ni\{N(CN)_2\}_2(NCS)_2]}$	2252, 2188, 2107,[c] 2058[c]		3.31	43
$\mathrm{[Ph_4As]_2[Ni\{N(CN)_2\}_2(NCS)_2]}$	2260sh, 2185, 2160sh, 2100[c]		3.38	43
$\mathrm{K_2[Co\{N(CN)_2\}_2(NCS)_2]}$	2214, 2160, 2085[c]	1.61, 1.695sh[b]		53
$\mathrm{K_2[Co\{N(CN)_2\}_2(NCO)_2]}$		1.54, 1.64, 1.75[b]		53
$\mathrm{[Ph_4P]_2[Co\{N(CN)_2\}_2(NCS)_2]}$	[a]	1.61, 1.65sh, 1.695sh[b]	4.83	53
$\mathrm{[Ph_4As]_2[Co\{N(CN)_2\}_2(NCS)_2]}$		1.61, 1.695[b]	4.58	53
$\mathrm{[Ph_4P]_2[Co\{N(CN)_2\}_2(NCO)_2]}$	2210, 2195[c], 2172	1.55, 1.67, 1.77[b]		53
$\mathrm{[Ph_4P]_2[Co\{N(CN)_2\}(NCS)_3]}$		1.61, 1.695sh[b]		53
$\mathrm{[Ph_4P]_2[Co\{N(CN)_2\}(NCO)_3]}$			4.65	53
$\mathrm{[Ni\{C(CN)_3\}_2(py)_4]}$	[a]	1.111, ~1.30sh, 1.786	3.12	37
$\mathrm{[Co\{C(CN)_3\}_2(py)_4]}$	2250, 2229, 2175			35
$\mathrm{[Cu\{C(CN)_3\}_2(py)_2]}$	2241, 2198			35
$\mathrm{[Ni\{C(CN)_3\}_2(py)_2]}$	[a]	1.087, ~1.35sh, 1.739	3.31	35,37
$\mathrm{[Co\{C(CN)_3\}_2(py)_2]}$	2250, 2203		5.09	35
$\mathrm{[Cu\{N(CN)_2\}_2(py)_2]}$	2240, 2172	~1.28sh, 1.52	2.21	44,45
$\mathrm{[Ni\{N(CN)_2\}_2(py)_2]}$	2255, 2200	1.042, ~1.33sh, 1.689, 2.717	3.14	35,37
$\mathrm{[Co\{N(CN)_2\}_2(py)_2]}$	2246, 2188	1.923, 2.062	5.16	35,38,39
$\mathrm{[Ni\{C(CN)_3\}_2(2\text{-}pic)_2]}$	2255, 2210			38
$\mathrm{[Co\{C(CN)_3\}_2(2\text{-}pic)_2]}$	2250, 2200			38
$\mathrm{[Cu\{N(CN)_2\}_2(2\text{-}pic)_2]}$	[a]	~1.23sh, 1.44	2.05	44
$\mathrm{[Ni\{N(CN)_2\}_2(2\text{-}pic)_2]}$	2254, 2208		2.86	38
$\mathrm{[Co\{N(CN)_2\}_2(2\text{-}pic)_2]}$	2246, 2190		5.06	37
$\mathrm{[Ni\{N(CN)_2\}_2(3\text{-}pic)_2]}$		1.031, ~1.35sh, 1.667, 2.667		

TABLE II (*Continued*)

Compound	$\nu(CN)$ (cm^{-1})	ν_{max} (μm)	μ_{eff}/μ_B	*Ref.*
$[Co\{N(CN)_2\}_2(3\text{-pic})_2]$		1.923, 2.00, 2.105	4.86	39
$[Cu\{C(CN)_3\}_2(4\text{-pic})_2]$	2250, 2205, 2190	~1.30sh, 1.41	1.91	44,54
$[Ni\{C(CN)_3\}_2(4\text{-pic})_2]$		1.081, ~1.39sh, 1.71	3.02	37
$[Co\{C(CN)_3\}_2(4\text{-pic})_2]$	2250, 2190	1.961, 2.174	4.90	39
$[Cu\{N(CN)_2\}_2(4\text{-pic})_2]$	[a]	~1.27sh, 1.51	1.81	44,54
$[Ni\{N(CN)_2\}_2(4\text{-pic})_2]$	2253, 2193	1.036, ~1.35sh, 1.667, 2.66	3.09	37
$[Co\{N(CN)_2\}_2(4\text{-pic})_2]$	2250, 2190			39
$[Cu\{C(CN)_3\}_2(2\text{-etpy})_2]$	2240, 2190	~1.30sh, 1.45	2.12	44
$[Cu\{N(CN)_2\}_2(2\text{-etpy})_2]$	[a]	~1.30sh, 1.46	1.95	44
$[Cu\{C(CN)_3\}_2(4\text{-etpy})_2]$	2245, 2200sh, 2185	~1.28sh, 1.45	1.83	44
$[Cu\{N(CN)_2\}_2(4\text{-etpy})_2]$	2250, 2185	~1.28sh, 1.51	1.95	44
$[Cu\{C(CN)_3\}_2(3,4\text{-lut})_2]$		~1.28sh, 1.45	1.83	44
$[Co\{N(CN)_2\}_2(2,3\text{-lut})_2]$	2246, 2191			39
$[Ni\{N(CN)_2\}_2(2,3\text{-lut})_2]$		0.966, ~1.39sh, 1.613, 2.632		37
$[Ni\{C(CN)_3\}_2(2,4\text{-lut})_2]$	2263, 2200, 2162sh	0.99, ~1.36sh, 1.647, 2.725	3.09	37
$[Co\{C(CN)_3\}_2(2,4\text{-lut})_2]$	2247, 2192	1.98, 2.081	5.09	39
$[Ni\{N(CN)_2\}_2(2,4\text{-lut})_2]$	2257, 2199	0.962, ~1.39, 1.60, 2.584	3.22	37
$[Co\{N(CN)_2\}_2(2,4\text{-lut})_2]$	[a]	1.961, 2.062	5.20	39
$[Cu\{C(CN)_3\}_2(3,4\text{-lut})_2]$	2245, 2200sh, 2185			
$[Cu\{N(CN)_2\}_2(3,4\text{-lut})_2]$	2250, 2185	~1.29sh, 1.45	2.03	44
$[Ni\{C(CN)_3\}_2(quin)_4]$	2250, 2200, 2150sh	1.026, ~1.39sh, 1.715, 2.778	3.34	37
$[Ni\{N(CN)_2\}_2(quin)_4]$	2250, 2185	0.98, ~1.38sh, 1.625, 2.618	3.38	37
$[Co\{N(CN)_2\}_2(quin)_4]$		1.961, 2.081	4.81	39
$[Cu\{C(CN)_3\}_2(quin)_2]$	2245, 2200sh, 2185	1.57	1.92	44
$[Cu\{N(CN)_2\}_2(quin)_2]$	2265, 2246, 2185	1.56	2.00	44
$[Ni\{N(CN)_2\}_2(quin)_2]$	2200–2180, 2155	0.971, ~1.35sh, 1.613, 2.632	3.16	37
$[Co\{N(CN)_2\}_2(quin)_2]$	2240, 2190	1.961, 2.062	4.99	39
$[Ni\{C(CN)_3\}_2(i\text{-quin})_4]$	2258, 2200	1.087, ~1.409sh, 1.754	3.18	37
$[Co\{C(CN)_3\}_2(i\text{-quin})_4]$		1.923, 2.272	5.14	39
$[Ni\{N(CN)_2\}_2(i\text{-quin})_4]$	2255, 2190	1.047, ~1.408sh, 1.699, 2.725	3.33	37
$[Co\{C(CN)_3\}_2(i\text{-quin})_2]$	[a]	1.942, 2.081	5.01	39
$[Ni\{N(CN)_2\}_2(i\text{-quin})_2]$		1.036, ~1.24sh, 1.667, 2.667	3.10	37
$[Co\{N(CN)_2\}_2(i\text{-quin})_2]$		1.934, 2.041	4.87	39
$[Cu\{N(CN)_2\}_2(2\text{-ampy})_2]$	2235, 2157	~1.33sh, 1.67	1.57	45
$[Cu\{N(CN)_2\}_2(3\text{-ampy})_2]$	2242, 2170	~1.35sh, 1.595	1.77	45
$[Cu\{N(CN)_2\}_2(4\text{-ampy})_2]$	2244, 2195, 2137	1.77	1.41	45
$[Ni\{N(CN)_2\}_2(2\text{-ampy})_2]$	2252, 2192	1.02, ~1.32sh, 1.63, ~2.63sh	3.14	45
$[Ni\{N(CN)_2\}_2(3\text{-ampy})_2]$	2258, 2194	1.02, ~1.35sh, 1.72, ~2.70sh	2.99	45
$[Ni\{N(CN)_2\}_2(4\text{-ampy})_2]$	2243, 2186	1.03, ~1.33sh, 1.67, ~2.21sh, 2.70	2.97	45
$[Cu\{N(CN)_2\}_2(2\text{-am-5-nipy})_2]$	2248, 2177	~1.20sh, 1.44	1.70	45
$[Ni\{N(CN)_2\}_2(2\text{-am-5-nipy})_2]$	2268, 2199	0.99, ~1.36sh, 1.68	3.26	45

TABLE II (*Continued*)

Compound	$\nu(CN)$ (cm^{-1})	ν_{max} (μm)	μ_{eff}/μ_B	*Ref.*
$[Co\{N(CN)_2\}_2(\text{2-am-5-nipy})_2]$	2254, 2186	0.94, ∼1.97sh, 2.12	4.85	45
$[Cu\{C(CN)_3\}_2(\text{3-CN-py})_2]$	2238^{d}, 2190, 2166	∼0.86sh, ∼1.28sh, 1.41		46
$[Ni\{C(CN)_3\}_2(\text{3-CN-py})_2]$	2246, 2232^{e}, 2197sh, 2183	1.07, ∼1.34sh, 1.74		46
$[Cu\{N(CN)_2\}_2(\text{3-CN-py})_2]$	2242, 2232sh^{e}, 2166	1.49		46
$[Ni\{N(CN)_2\}_2(\text{3-CN-py})_2]$	2249, 2232^{e}, 2185	1.03, ∼1.34sh, 1.63, ∼2.68sh		46
$[Cu\{C(CN)_3\}_2(\text{4-CN-py})_2]$	2246sh^{e}, 2238, 2200, 2166	∼0.88sh, ∼1.29sh, 1.44		46
$[Ni\{C(CN)_3\}_2(\text{4-CN-py})_2]$	2243^{d}, 2202, 2185	1.08, ∼1.34sh, 1.73		46
$[Cu\{N(CN)_2\}_2(\text{4-CN-py})_2]$	2238^{d}, 2208sh, 2166	1.46		46
$[Ni\{N(CN)_2\}_2(\text{4-CN-py})_2]$	2256, 2238sh^{e}, 2187	1.02, ∼1.35sh, 1.69		46
α-$[Cu\{C(CN)_3\}_2(pz)_2]$	2247, 2193	1.58	1.62	47
β-$[Cu\{C(CN)_3\}_2(pz)_2]$	2247, 2193, 2174, 2162	1.64		47
$[Cu\{C(CN)_3\}_2(pz)_3]$	2253, 2209, 2195, 176, 2165	1.48, ∼1.69sh	1.71	47
$[Cu\{C(CN)_3\}_2(pz)_4]$	2190, 2181, 2169	1.46, ∼1.63sh	1.71	47
$[Ni\{C(CN)_3\}_2(pz)_2]$	2248, 2194, 2161	1.08, 1.79, ∼2.78sh	3.04	21
$[Cu\{N(CN)_2\}_2(pz)_2]$	2240, 2182	1.575	1.93	56
$[Ni\{N(CN)_2\}_2(pz)_2]$	2248, 2179, 2139	1.04, 1.72, 2.78	2.86	21
$[Co\{N(CN)_2\}_2(pz)_2]$	2245, 2180	0.94, ∼1.86sh, ∼1.97sh, 2.12	5.11	21
$[Cu\{C(CN)_3\}_2(mpz)_2]$	2247, 2195, 2170sh	∼1.15sh, 1.54	1.78	21
$[Cu\{N(CN)_2\}_2(mpz)_2]$	2240, 2173	∼1.14sh, 1.47	1.93	21
$[Cu\{C(CN)_3\}_2(dmpz)_2]$	2249, 2190	∼1.22sh, 1.56	1.83	21
$[Cu\{N(CN)_2\}_2(dmpz)_2]$	2260, 2250, 2185	∼1.19sh, 1.52	2.19	21
$[Cu\{C(CN)_3\}_2(tmpz)_2]$	2250, 2222, 2196, 2191sh	∼1.24sh, 1.58	1.55	21,57
$[Ni\{C(CN)_3\}_2(tmpz)_2]$	2250, 2200	1.05, 1.72, ∼2.70sh	2.93	21
$[Cu\{N(CN)_2\}_2(tmpz)_2]$	2258, 2234, 2182, 2149	∼1.15sh, 1.45	1.65	21,57
$[Ni\{N(CN)_2\}_2(tmpz)_2]$	2250, 2180, 2150sh	1.12, 1.69, 2.76	3.16	21
$[Cu\{N(CN)_2\}_2(inz)_2]$	2244, 2175	∼1.15sh, 1.53	1.97	21
$[Cu\{C(CN)_3\}_2(\text{4-Cl-pz})_2]$	2250, 2189	1.63		55
$[Cu\{C(CN)_3\}_2(\text{4-Br-pz})_2]$	2244, 2188	∼1.28sh, 1.44, 2.42		55
$[Ni\{C(CN)_3\}_2(\text{4-Br-pz})_2]$	2259, 2225, 2190	∼0.70sh, 1.03, ∼1.37sh, 1.73, ∼2.26sh, 2.64		55
$[Co\{C(CN)_3\}_2(\text{4-Br-pz})_2]$	2248, 2187	0.99, ∼1.92sh, ∼2.27sh		55
$[Cu\{N(CN)_2\}_2(\text{4-Br-pz})_2]$	2264, 2192	1.56		55
$[Ni\{N(CN)_2\}_2(OMNA)_2]$	2266, 2200			59
$[Co\{N(CN)_2\}_2(OMNA)_2]$	2260, 2190			59
$[Cu\{N(CN)_2\}_2(en)_2]$	2255, 2195, 2170sh	1.08, 1.74^{b}		60
$[Ni\{N(CN)_2\}_2(en)_2]$	2235, 2175	1.08, 1.75, 2.82^{b}		60
$[Co\{N(CN)_2\}_2(en)_2]$	2220, 2190, 2165	1.075, 2.00^{b}		60
$[Cu\{N(CN)_2\}_2(bpy)_2]$	2235, 2180	1.28		60
$[Ni\{N(CN)_2\}_2(bpy)_2]$	2230, 2180	1.11, 1.8		60
$[Co\{N(CN)_2\}_2(bpy)_2]$	2230, 2185	1.00, 2.04		60
$[Cu\{N(CN)_2\}_2(phen)_2]$	2255, 2195, 2170	1.32		60
$[Ni\{N(CN)_2\}_2(phen)_2]$	2240, 2185	1.10, 1.75		60
$[Co\{N(CN)_2\}_2(phen)_2]$	2240–2225, 2185	1.00, 2.05		60
$[Cu\{N(CN)_2\}_2(DMSO)_2]$	2243, 2170			60

TABLE II (*Continued*)

Compound	$\nu(CN)$ (cm^{-1})	ν_{max} (μm)	μ_{eff}/μ_B	*Ref.*
$[Ni\{N(CN)_2\}_2(DMSO)_2]$	2263, 2200		3.09	61
$[Co\{N(CN)_2\}_2(DMSO)_2]$	2255, 2192		4.90	61
$[Cu\{C(CN)_3\}_2(HMPA)_4]$	2252, 2185, 2150			62
$[Ni\{C(CN)_3\}_2(HMPA)_2]$	2252, 2212, 2190, 2165			62
$[Co\{C(CN)_3\}_2(HMPA)_2]$	2246, 2195, 2185			62
$[Ni\{C(CN)_3\}(NO)]$	2218			63
$[Co\{C(CN)_3\}(NO)_2]$	2268, 2220sh, 2206			63
$[Co\{C(CN)_3\}(NO)_2(PPh_3)]$	2218, 2173			63
$[Co\{C(CN)_3\}(NO)_2(PCy_3)]$	2230, 2184, 2173			63
$[Ni\{C(CN)_3\}(NO)(PCy_3)]$	2228, 2192, 2180			63
$[Ni\{C(CN)_3\}(NO)(PCy_3)_2]$	2217, 2179sh, 2166			63
$[Ni\{C(CN)_3\}(NO)(C_2H_4)(PPh_3)_2]$	2222, 2173			63
$[Cu\{C(CN)_3\}_2(iz)_2]$	2235, 2190, 2170, 2150sh	~1.10sh, 1.52		64
$[Cu\{C(CN)_3\}_2(2\text{-}meiz)_4]$	2239, 2218sh, 2185, 2169	~1.40sh, 1.66		64
$[Cu\{C(CN)_3\}_2(2\text{-}meiz)_2]$	2245, 2185, 2141sh	~1.21sh, 1.48		64
$[Cu\{C(CN)_3\}_2(4\text{-}meiz)_4]$	2230, 2171, 2132	~1.38sh, 1.71		64
$[Cu\{C(CN)_3\}_2(4\text{-}meiz)_2]$	2250, 2202sh, 2188	~0.92sh, 1.26sh, 1.49		64
$[Ni\{C(CN)_3\}_2(iz)_2]$	2259, 2210sh, 2200	1.07, ~1.20sh, ~1.35sh, 1.75, ~2.74sh		64
$[Ni\{C(CN)_3\}_2(2\text{-}meiz)_2]$	2253, 2210, 2197	1.03, ~1.19sh, ~1.36sh, 1.65, 2.70		64
$[Ni\{C(CN)_3\}_2(4\text{-}meiz)_2]$	2254, 2209, 2192	1.05, ~1.21sh, ~1.36sh, 1.72, ~2.72sh		64
$[Co\{N(CN)_2\}_2(iz)_2]$	2246s, 2185vs	0.94, 1.79sh, 1.97sh, 2.14		49
$[Co\{C(CN)_3\}_2(iz)_2]$	2247m, 2198vs	1.00, 1.73sh, 1.83, 2.07sh, 2.22		49
$[Co\{N(CN)_2\}_2(2\text{-}meiz)_2]$	2235sh, 2212vs, 2165vs, 2139sh	0.865, 1.74, 1.85sh, 2.45sh		49
$\alpha\text{-}[Co\{C(CN)_3\}_2(2\text{-}meiz)_2]$	2223, 2204, 2164sh	1.02, 1.72sh, 1.84, 2.02sh, 2.25		49
$\beta\text{-}[Co\{C(CN)_3\}_2(2\text{-}meiz)_2]$	2243, 2192, 2147	0.87, 1.000sh, 1.70, 1.78sh, 1.87sh, 2.26sh		49
$[Co\{N(CN)_2\}_2(4\text{-}meiz)_2]$	2236, 2171	0.81sh, 0.90, 1.03sh, 1.75, 1.88sh, 2.15sh		49
$\alpha\text{-}[Co\{C(CN)_3\}_2(4\text{-}meiz)_2]$	2247, 2188, 2154sh, 2141sh	1.03, 1.70sh, 1.81, 2.04sh, 2.22		49
$\beta\text{-}[Co\{C(CN)_3\}_2(4\text{-}meiz)_2]$	2242, 2192, 2158sh, 2142sh	0.79sh, 0.92, 1.08sh, 1.74, 1.90sh, 2.25		49
$[Cu\{C(CN)_3\}_2(biz)_2]$	2233, 2180sh, 2163	1.21sh, 1.36sh, 1.61	1.55	48
$[Cu\{C(CN)_3\}_2(2\text{-}mebiz)_2]$	2240, 2190sh, 2178	1.26sh, 1.61	1.78	48
$[Ni\{C(CN)_3\}_2(biz)_2]$	2240, 2189, 2167	0.80sh, 0.99, 1.20sh, 1.70, 2.35, 2.81sh	3.05	48
$[Ni\{C(CN)_3\}_2(2\text{-}mebiz)_2]$	2259, 2210, 2199	1.03, 1.71	2.64	48
$[Co\{C(CN)_3\}_2(biz)_2]$	2234, 2186, 2162	0.88, 1.71, 1.87sh, 2.06, 2.20sh	4.74	48
$[Co\{C(CN)_3\}_2(2\text{-}mebiz)_2]$	2255, 2197	0.97, 1.33sh, 1.89sh, 2.22sh	4.74	48

TABLE II (*Continued*)

Compound	$\nu(CN)$ (cm^{-1})	ν_{max} (μm)	μ_{eff}/μ_B	*Ref.*
$[Co\{N(CN)_2\}_2(2\text{-mebiz})_2]$	2280[a], 2245, 2183	0.73sh, 0.91, 1.30, 1.64sh, 1.84sh, 2.08	3.71	48
$[Cu\{N(CN)_2\}_2(biz)_2]$	2233, 2158	1.19sh, 1.33sh, 1.67	1.82	58
$[Cu\{N(CN)_2\}_2(2\text{-mebiz})_2]$	2255, 2237	1.19sh, 150	1.91	58
$[Cu\{N(CN)_2\}_2(2\text{-etbiz})_2]$	2235, 2167	1.21sh, 1.29sh, 160	1.94	58
$[Ni\{N(CN)_2\}_2(biz)_2]$	2243, 2180	1.00, 1.18sh, 1.34sh, 1.65, 2.70	3.07	58
$[Ni\{N(CN)_2\}_2(2\text{-mebiz})_2]$	2251, 2178	0.98, 1.61, 2.63	3.20	58
$[Ni\{N(CN)_2\}_2(2\text{-etbiz})_2]$	2240, 2205sh, 2197, 2172	0.90, 1.63, 2.08sh, 2.60sh	3.20	58
$[Co\{N(CN)_2\}_2(biz)_2]$	2235, 2165	0.89, 1.72, 1.89sh, 2.13sh	4.84	58
$[Co\{N(CN)_2\}_2(2\text{-etbiz})_2]$	2233, 2167	0.73sh, 0.88, 1.28, 1.84sh, 2.07	4.99	58
$[Cu\{C(CN)_3\}_2(4\text{-NO-pz})_2]$	2262, 2210sh, 2192	1.20sh, 1.55		65
$[Ni\{N(CN)_2\}_2(4\text{-NO-pz})_2]$	2257, 2190	1.04, 1.35sh, 1.72		65
α-$[Cu\{N(CN)_2\}_2(iz)_2]$	2240, 2180	1.65, 1.42sh, 0.91sh	1.77	66
β-$[Cu\{N(CN)_2\}_2(iz)_2]$	2240, 2180	1.61, 1.36sh, 0.91sh	1.93	66
$[Cu\{N(CN)_2\}_2(1\text{-meiz})_2]$	2279, 2230, 2164	1.21sh, 1.31sh, 1.54		50
$[Ni\{N(CN)_2\}_2(iz)_2]$	2278, 2237, 2203, 2195	1.07, 1.33sh, 1.74, 2.82		50
$[Ni\{N(CN)_2\}_2(1\text{-meiz})_2]$	2283, 2250, 2190, 2168	1.02, 1.70, 2.74		50
$[Co\{N(CN)_2\}_2(1\text{-meiz})_2]$	2280, 2236, 2185, 2176	0.91, 1.87sh, 2.12		50

[a] See Table I. [b] Solution spectrum. [c] The ν(CN) vibration of the NCS or NCO ligand. [d] The band contains the ν(CN) vibration of cyanopyridine. [e] The ν(CN) mode of cyanopyridine.

(ii) The compound $[Ph_3MeAs]_2[Co\{N(CN)_2\}_4]$ was prepared by addition of $[Ph_3MeAs][Co\{N(CN)_2\}_3]$ and $[Ph_3MeAs]N(CN)_2$ in acetone solution.

(iii) The compound $[Me_4N]_2[Cu\{N(CN)_2\}_4]$ can be obtained by reaction of $CuBr_2$, $[Me_4N]Br$ and $Ag[N(CN)_2]$.

3.3 Synthesis of Compounds with Mixed Pseudohalide Anions

(i) Analogous to the synthesis of $[M\{N(CN)_2\}_4]^{2-}$ but instead of $[N(CN)_2]^-$ the corresponding salts of $[NCO]^-$ or $[NCS]^-$ are used.

(ii) Dicyanamide of metals were suspended in a solution of alkaline cyanate or thiocyanate in dry acetone.

(iii) Alkaline cyanate or thiocyanate is treated in acetone with a transition metal salt and $[Ph_4P]N(CN)_2$ or $[Ph_4As]N(CN)_2$.

3.4 Synthesis of Tricyanomethanide and Dicyanamide Complexes with Neutral Ligands

(i) Treating water solution of a transition metal salt with the alkali metal tricyanomethanide or dicyanamide and corresponding neutral ligands at room temperature, at higher temperatures or under reflux.

(ii) Treating the transition metal salt with alkaline tricyanomethanide or dicyanamide in methanol or ethanol solution and in water–methanol mixture.
(iii) Substitution of Cl^- in transition metal complexes by treating with $[C(CN)_3]^-$ or $[N(CN)_2]^-$ in methanol solution.
(iv) Controlled thermal decomposition of complexes with a larger number of neutral ligands.
(v) Treating metal tricyanomethanides or dicyanamides with corresponding neutral ligands.
(vi) Dissolving transition metal tricyanomethanides or dicyanamides in a neutral ligand and precipitating the complex by addition of non-polar solvent.

4 RESULTS OF STRUCTURE STUDIES

4.1 X-ray Analyses

Crystallographic data for tricyanomethanide and dicyanamide complexes of Cu(II), Ni(II) and Co(II), solved by single-crystal X-ray analysis, are summarized in Table III.

The first compound of a non-linear pseudohalide studied by X-ray crystallography was $[Cu\{C(CN)_3\}_2]$.[36] More recently crystal structures of $[Mn\{C(CN)_3\}_2]$[16] and $[Zn\{C(CN)_3\}_2]$[67] were published. In all these compounds each M(II) atom is bonded to six $C(CN)_3$ groups and each $C(CN)_3$ group bridges between three M(II) atoms. The crystal structures of the last two compounds were described as two interpenetrating rutile-type nets and similar structures were attributed also to tricyanomethanides of Cu(II), Ni(II) and Co(II).[14]

Two research groups[13,14] reported the structures of $[M\{N(CN)_2\}_2]$, where M = Cu, Ni and Co. These compounds are isostructural and have each dicyanamide ion coordinated to three metal atoms through two nitrile and one amide nitrogen atoms (Figure 1). The structures contain linear ribbons which link approximately orthogonally through amide nitrogens completing in axial positions the 4 + 2 coordination of the M(II) atoms. The Cu(II) compound shows appreciable Jahn–Teller distortion with the two axial amide nitrogens considerably further from the Cu(II) atom than the four equatorial nitrile nitrogens.

The compound β-$[Co\{N(CN)_2\}_2]$ is a structural isomer of the above-mentioned Co(II) compound, denoted α.[40] The β-isomer is isostructural with β-$[Zn\{N(CN)_2\}_2]$, the structure of which, as well as the structure of 0.12% β-$[Co,Zn\{N(CN)_2\}_2]$, was solved by X-ray crystallography.[15]

TABLE III Basic crystallographic data for tricyanomethanide and dicyanamide complexes

Compound	*Crystallographic system*	*Space group*	*a* (Å) *b* (Å) *c* (Å)	α (°) β (°) γ (°)	*Z*	*R*	*M–N(X)*	*M–N(L)*	*Ref.*
$[Cu\{C(CN)_3\}_2]$	Orthorhombic	*Pmna*	7.176(5) 5.471(5) 10.753(5)		2	0.099	1.98(1) 2.49(1)		36
$[Cu\{N(CN)_2\}_2]$	Orthorhombic	*Pnnm*	6.120(1) 7.339(1) 7.173(1)		2	0.0293	1.979(3) 2.473(4)		13
$[Ni\{N(CN)_2\}_2]$[a]	Orthorhombic	*Pnnm*	5.980(1) 7.107(1) 7.393(1)		2				13
α-$[Co\{N(CN)_2\}_2]$[b]	Orthorhombic	*Pnnm*	5.970(1) 7.060(1) 7.406(1)		2	0.0182	2.096(1) 2.153(2)		13
β-$[Co\{N(CN)_2\}_2]$[c]	Orthorhombic	*Pnma*	7.6070(3) 7.5828(4) 7.5882(4)		4	0.0273	[d]		15
$[Cu\{C(CN)_3\}(pz)_4][C(CN)_3]$	Monoclinic	$P2_1/c$	9.568(4) 16.692(7) 14.957(9)	94.05(4)	4	0.0369	2.373(7) 2.500(7)	1.979(6)–2.007(5)	47
$[Cu\{C(CN)_3\}_2(pz)_3]$	Triclinic	*P*1	7.607(4) 8.942(6) 16.027(10)	95.95(6) 90.83(5) 106.88(5)	2	0.0374	1.985(4) 2.420(4) 2.472(4)	1.981(4)–1.987(3)	47
$[Cu\{C(CN)_3\}_2(2\text{-meiz})_2]$	Monoclinic	$P2_1/c$	9.619(3) 13.797(5) 7.049(4)	92.13(4)	4	0.0307	2.017(2) 2.441(2)	1.973(2)	64
$[Cu\{N(CN)_2\}_2(phen)_2]$	Monoclinic	$P2_1/c$	8.756(4) 14.611(6) 18.979(8)	101.21(4)	4	0.0405	1.951(3) 2.365(3)	2.008(2)–2.045(3) 2.312(3)	68
$[Cu\{N(CN)_2\}(phen)_2][C(CN)_3]$	Monoclinic	$P2_1/n$	10.080(7) 12.972(7) 19.874(13)	100.22(6)	4	0.0487	1.982(4)	1.977(4)–2.112(4)	71

$[Cu\{C(CN)_3\}(bpy)_2][C(CN)_3]$	Monoclinic	$P2_1/c$	14.530(6) 13.290(6) 14.231(6)	110.31(3)	4	0.036	1.993(3)	1.954(2)–2.104(3)	72
$[Ni\{N(CN)_2\}_2(5\text{-meiz})_2]$	Monoclinic	$C2/m$	17.187(4) 7.302(2) 6.666(2)	110.58(2)	8	0.0317	2.102(2)	2.064(3)	69
$[Ni\{N(CN)_2\}_2(5\text{-meiz})_4]$	Triclinic	$P1$	9.448(3) 9.918(3) 15.173(5)	107.85(2) 93.67(2) 104.74(2)	2	0.0370	2.114(2) 2.120(2)	2.090(2) 2.107(2) 2.115(2)	70
α-$[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$	Orthorhombic	$P2na$	7.393(2) 9.999(5) 13.557(10)		4	0.0492	2.155(2)	2.103(2)	49
$[Ph_4P]_2[Co\{N(CN)_2\}_4]$	Monoclinic	$C2/c$	23.430(6) 7.589(12) 28.534(4)	105.65(2)	8	0.0464	2.091(3)–2.177(3)		73

[a] Powder X-ray diffraction. [b] Temperature 150(2) K. [c] A sample of 0.12% β-$[Co,Zn\{N(CN)_2\}_2]$. [d] Only values for the isomorphous structure of $[Zn\{N(CN)_2\}_2]$ are reported: 1.936(4)–1.960(3) Å.

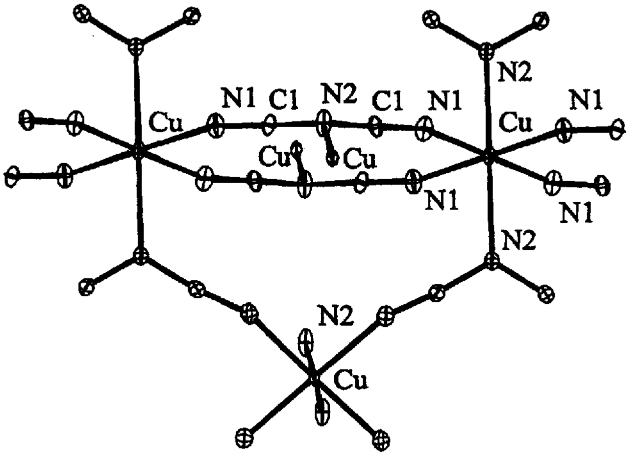


FIGURE 1 Coordination of the $[N(CN)_2]^-$ ion in $[Cu\{N(CN)_2\}_2]$.

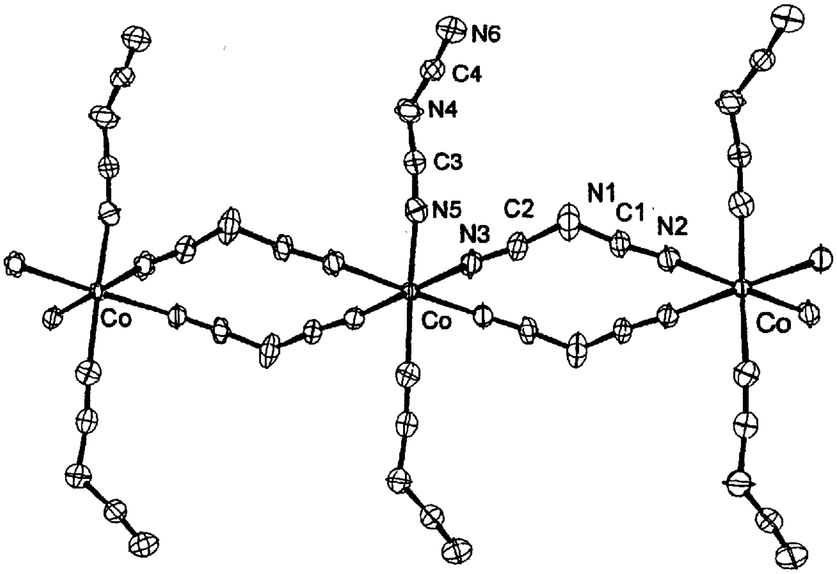


FIGURE 2 Structure of the sheet in β-$[Co\{N(CN)_2\}_2]$.

These structures (Figure 2) consist of tetrahedrally coordinated metal atoms, connected by dicyanamide ligands *via* their nitrile nitrogens to give infinite sheets. Thus, the amide nitrogens are not used for coordination.

The crystal structures of $[Cu\{C(CN)_3\}(pz)_4][C(CN)_3]$ and $[Cu\{C(CN)_3\}_2(pz)_3]$ are rather unique.[47] The structure of the former compound (Figure 3)

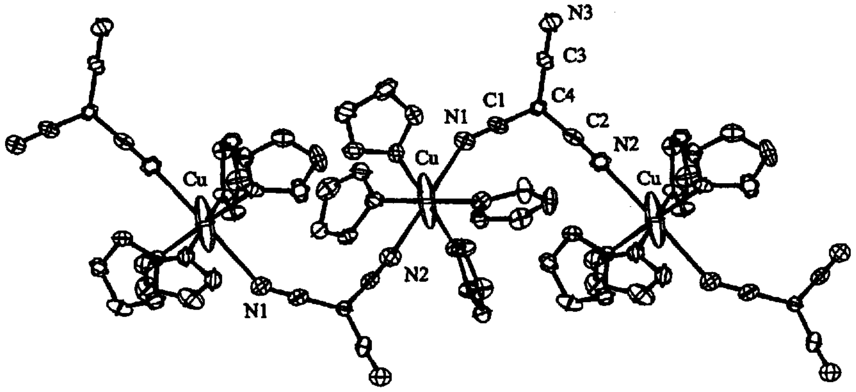


FIGURE 3 Structure of the chain in $[Cu\{C(CN)_3\}(pz)_4][C(CN)_3]$.

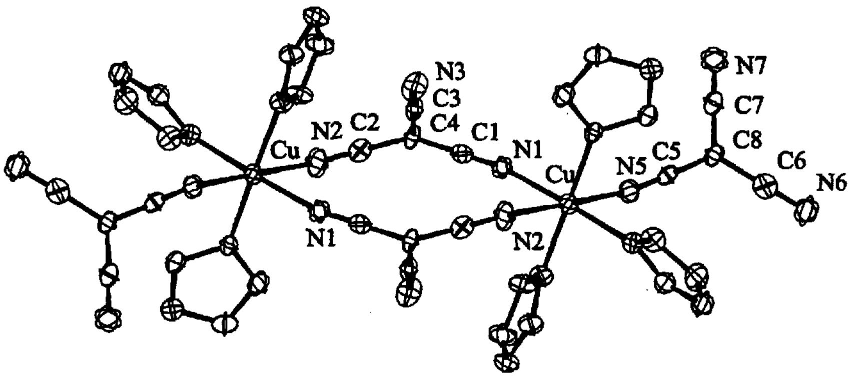


FIGURE 4 Structure of dimeric species in $[Cu\{C(CN)_3\}_2(pz)_3]$.

consists of polymeric one-dimensional chains formed by $[Cu(pz)_4]^{2+}$ cations linked together by one, bridging $C(CN)_3$ group, while the second is anionic. The structure of the latter compound (Figure 4) contains discrete dimeric species formed by two complex molecules bridged by one $C(CN)_3$ group. Cu(II) coordination is completed by another monodentate $C(CN)_3$ ligand. The $C(CN)_3$ ligand is rather rigid and correlation may be seen between the $Cu-N_{ax}$ axial distances and the $Cu-N_{ax}-C$ angle for both crystal structures:

Compound	*Cu–N*$_{ax}$ (Å)	*Cu–N*$_{ax}$*–C* (°)
$[Cu\{C(CN)_3\}(pz)_4][C(CN)_3]$	2.373(7), 2.500(7)	173.7(7), 148.9(6)
$[Cu\{C(CN)_3\}_2(pz)_3]$	2.420(4), 2.472(4)	156.6(4), 151.6(4)

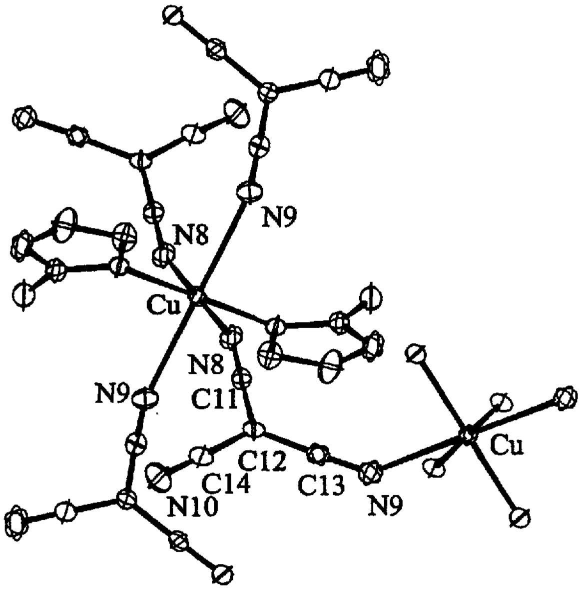


FIGURE 5 Molecular structure of $[Cu\{C(CN)_3\}_2(2\text{-meiz})_2]$ and connection of two coordination polyhedra.

The crystal structure of $[Cu\{C(CN)_3\}_2(2\text{-meiz})_2]$ (Figure 5) is polymeric and bidentate bridging $C(CN)_3$ groups link Cu(II) atoms into two-dimensional networks which are connected through hydrogen bonds.[64] On the other hand, the crystal structure of $[Cu\{N(CN)_2\}_2(phen)_2]$ is made up of discrete molecules (Figure 6). The Cu(II) atom is coordinated by two phen molecules and by the $N(CN)_2$ groups in a *cis*-arrangement. This structure is rather unusual since in Cu(II) compounds containing two phen molecules and two univalent anions the coordination polyhedra are mostly in the form of distorted trigonal bipyramids (or tetragonal pyramids) with an uncoordinated second anion.[68]

In the compounds $[Ni\{N(CN)_2\}_2(5\text{-meiz})_2]$[69] and α-$[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$[49] the central atom is nearly octahedrally coordinated by two *trans* tertiary nitrogens of the L ligands and four nitrile nitrogens from the pseudohalide anions which form the equatorial plane (Figures 7 and 8). The basic structural units are linked by bidentate bridging pseudohalide groups into polymeric one-dimensional chains. The compound $[Ni\{N(CN)_2\}_2(5\text{-meiz})_4]$[70] has a monomeric molecular structure consisting of practically regular octahedral complexes with unidentate, mutually *trans*-located $N(CN)_2$ groups (Figure 9).

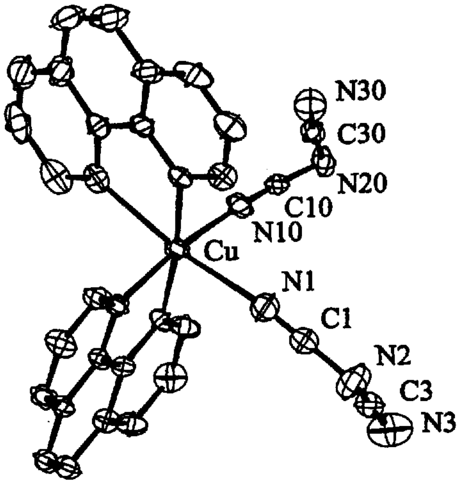


FIGURE 6 Molecular structure of [Cu$\{N(CN)_2\}_2$(phen)$_2$].

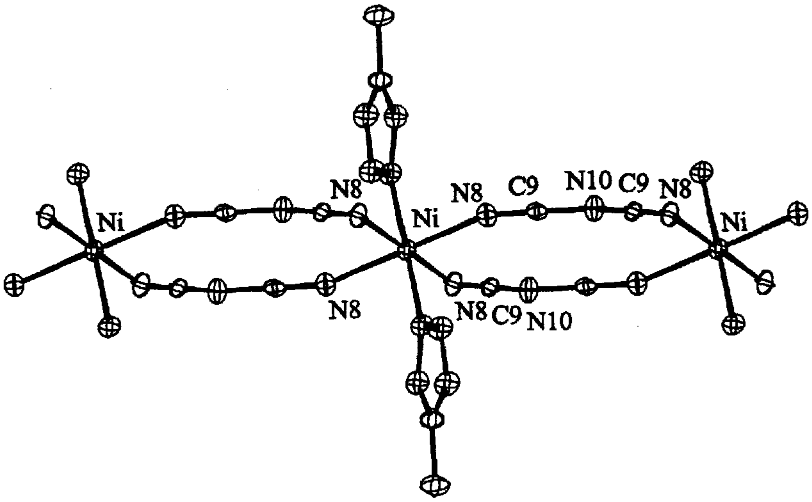


FIGURE 7 Molecular structure of [Ni$\{N(CN)_2\}_2$(5-meiz)$_2$] and connection of two coordination polyhedra.

The crystal structures of [Cu$\{N(CN)_2\}$(phen)$_2$][C(CN)$_3$][71] and [Cu$\{C(CN)_3\}$(bpy)$_2$][C(CN)$_3$][72] contain discrete [CuXL$_2$]$^+$ cations (L = phen, bpy) in which the Cu(II) atom is five-coordinated by nitrogen atoms of the two L molecules and the X$^-$ anions (Figures 10 and 11).

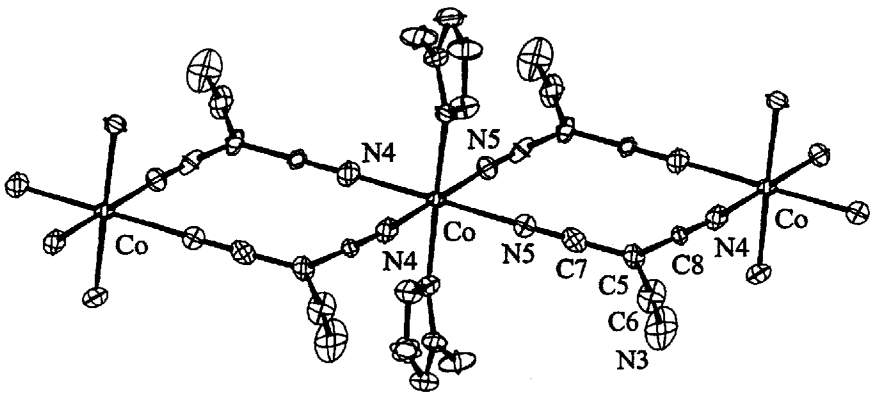


FIGURE 8 Molecular structure of α-$[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$ and connection of two coordination polyhedra.

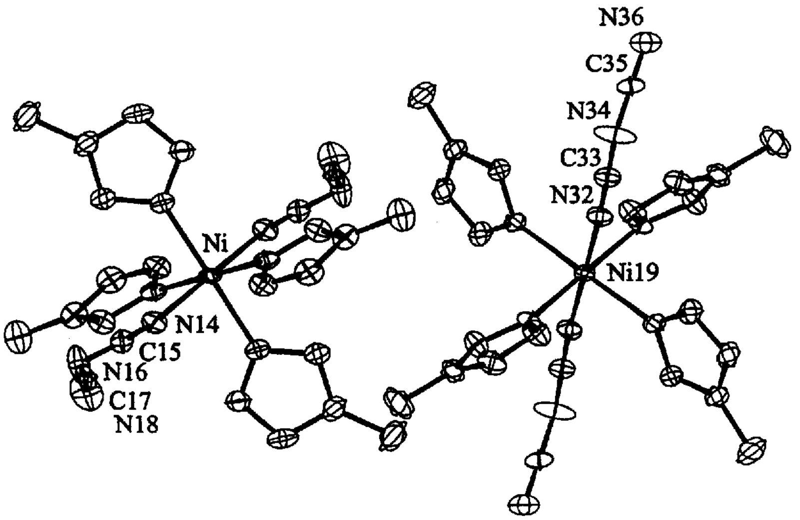


FIGURE 9 Molecular structure of two symmetrically independent molecules in $[Ni\{N(CN)_2\}_2(5\text{-meiz})_4]$.

The coordination polyhedra in both cases are distorted trigonal bipyramids. In the compound $[Ph_4P]_2[Co\{N(CN)_2\}_4]$ infinite chains (Figure 12) are present, in which the Co(II) atoms are doubly bridged by $N(CN)_2$ groups using nitrile nitrogens. Pseudo-octahedral coordination of each Co(II) atom is

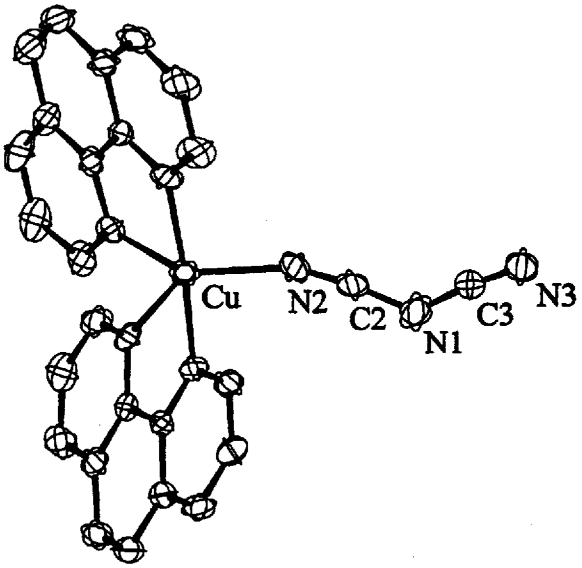


FIGURE 10 Molecular structure of $[Cu\{N(CN)_2\}(phen)_2]^+$.

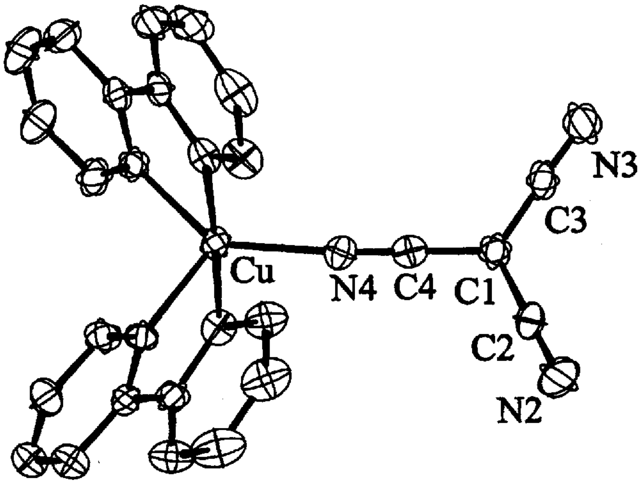


FIGURE 11 Molecular structure of $[Cu\{C(CN)_3\}(bpy)]^+$.

completed by two nitrile nitrogens of monodentate $N(CN)_2$ ligands.[73] In Tables IV and V bond lengths and angles of tricyanomethanide and dicyanamide in various compounds, for which X-ray crystallographic studies were carried out, are summarized.

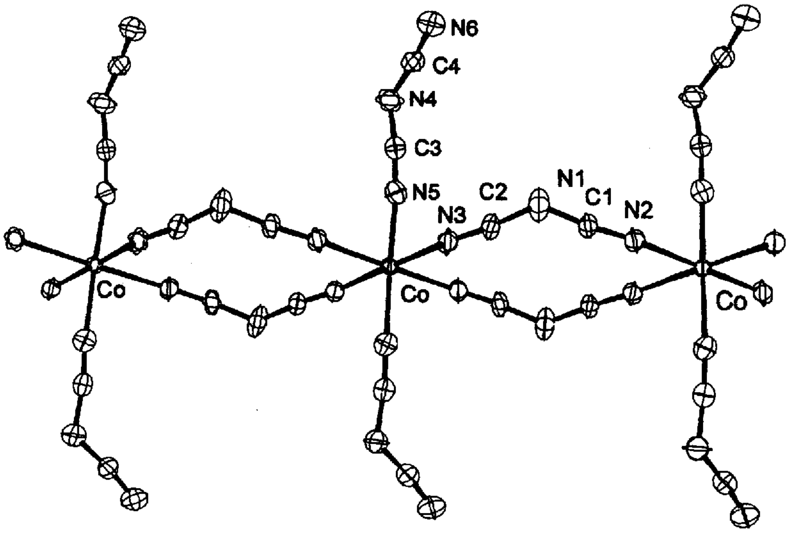


FIGURE 12 Structure of the chain in $[Ph_4P]_2[Co\{N(CN)_2\}_4]$.

5 ELECTRONIC PROPERTIES

5.1 Electronic d–d-Spectra

Electronic d–d-spectra of coordination compounds of Ni(II) and Co(II) enable one to determine the local environment of the central atom as well as the electronic parameters (ligand field strength, nephelauxetic ratio) characterizing the M(II)–ligand bond.[93] In the case of Cu(II) complexes, information from the d–d spectra is more limited and less unequivocal. However, at least an approximate assignment of the geometry of the coordination polyhedron is possible. Often one can judge the degree of distortion, characteristic of Cu(II) complexes.[94,96] Electronic spectra of all tricyanomethanide and dicyanamide complexes of Ni(II) exhibit three or two d–d bands within the range 0.90–1.12, 1.60–1.80 and 2.55–2.82 μm^{-1}. These bands indicate unequivocally an octahedral coordination sphere and in order of increasing energy they can be assigned to the transitions $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$. In some cases the last band is not noticed because it is overlapped by a strong charge transfer or ligand transition band. Splitting of the NIR band, indicating more extensive tetragonal distortion of the octahedral complex, appears in some cases.[64] Often a more or less developed shoulder appears around 1.35 μm^{-1}, arising from the spin-forbidden transition $^1E_g \leftarrow {}^3A_{2g}$.

TABLE IV Bond lengths (Å) and angles (°) of tricyanomethanide in various compounds

Compound	*M–N*	*N≡C*	*C–C*	*C–C*	*C≡N*	*N–M*	*–N–C–C*	*C–C–C*$_{min/max}$	*C–C–N*	*Bonding mode*	*Ref.*
$Na[C(CN)_3]$	2.373	1.145(3)	1.405(3)	1.411(3) 1.409(2)	1.151(3) 1.164(2)	2.471 2.542	178.7(3)	119.2(2) 120.7(2)	179.0(2) 179.8(2)	Ionic	27
$(ET)_2[C(CN)_3]$		1.158(6)	1.407(5)	1.413(3)	1.161(3)		180	119.7(3) 120.2(2)	178.8(3)	Ionic	74
$Ag[C(CN)_3]$	2.11(6)	1.10(9)	1.54(9)	1.41(7)	1.16(5)	2.26(4)	173(13)	118(4) 124(7)	173(7)	Tridentate	75
$Me_3Sn\{C(CN)_3\} \cdot H_2O$	2.363(11)	1.162(16)	1.371(17)	1.401(17) 1.423(16)	1.140(16) 1.142(14)		178.9(15)	119.1(10) 120.6(11)	178.2(14) 176.9(13)	Monodentate	76
$Me_2Tl\{C(CN)_3\}$	2.67(3)	1.21(4)	1.33(3)	1.42(4)	1.13(4)	2.91(1)	176.4(31)	118.0(31) 121.0(16)	180	Tridentate	51
$Hg_2\{C(CN)_3\}_2$[a]	2.405(9)	1.160(13)	1.421(13)	1.387(11) 1.418(12)	1.116(11) 1.116(11)	2.507(9)	176.7(1)	119.6(1) 120.3(1)	176.9(1) 179.2(1)	Bidentate	77
$Hg_2\{C(CN)_3\}_2$	2.282(8)	1.156(11)	1.360(11)	1.409(11) 1.424(13)	1.138(11) 1.156(11)	2.434(8) 2.440(9)	178.0(1)	117.4(1) 123.9(1)	178.4(1) 178.2(1)	Tridentate	77
$[Au\{C(CN)_3\}(PPh_3)_2]$	2.726(11)	1.14(2)	1.38(2)	1.44(2) 1.39(2)	1.12(2) 1.16(2)		177(2)	118(1) 122(1)	177(2) 179(2)	Monodentate	78
$[CuCN(phen)_2]C(CN)_3$		1.072(6)	1.405(8)	1.452(7) 1.463(9)	1.098(6) 1.188(8)		172.9(7)	118.8(6) 120.9(5)	173.4(7), 176.1(6)	Ionic	79
$[CuNCS(phen)_2]C(CN)_3$		1.147(6)	1.387(6)	1.395(6) 1.400(6)	1.145(5) 1.143(5)		178.9(6)	119.2(4) 121.3(4)	177.8(4) 178.6(5)	Ionic	80
$[Cu\{N(CN)_2\}(phen)_2]$-$C(CN)_3$		1.123(6)	1.394(8)	1.374(7) 1.395(7)	1.135(7) 1.132(6)		179.2(7)	117.9(5) 122.1(5)	177.6(6) 179.7(5)	Ionic	71
$[Cu\{C(CN)_3\}(bpy)_2]$-$C(CN)_3$[a]	1.993(3)	1.138(4)	1.393(5)	1.397(5) 1.391(5)	1.131(5) 1.132(5)		178.3(4)	119.1(3) 121.0(3)	179.6(5) 178.8(4)	Monodentate	72
$[Cu\{C(CN)_3\}(bpy)_2]$-$C(CN)_3$		1.139(6)	1.387(6)	1.138(5) 1.131(4)	1.392(5) 1.384(5)		179.1(6)	119.6(4) 120.7(4)	177.8(5) 178.4(4)	Ionic	72
$[CuC(CN)_3(pz)_4]C(CN)_3$	2.373(7)	1.133(6)	1.395(6)	1.384(7) 1.412(6)	1.155(6) 1.141(5)	2.500(7)				Bidentate	47
$[Cu\{C(CN)_3\}_2(pz)_3]$[a]	1.985(4)	1.147(6)	1.404(6)	1.404(6) 1.384(6)	1.143(5) 1.141(6)	2.472(4)				Bidentate	47

TABLE IV (*Continued*)

Compound	*M–N*	*N≡C*	*C–C*	*C–C*	*C≡N*	*N–M*	*–N–C–C*	*C–C–C*$_{min/max}$	*C–C–N*	*Bonding mode*	*Ref.*
[Cu{C(CN)$_3$}$_2$(pz)$_3$]	2.420(4)	1.146(5)	1.397(7)	1.394(6)	1.142(7)					Monodentate	47
				1.394(6)	1.147(7)						
[Re{C(CN)$_3$}(CO)$_5$]	2.112(9)	1.144(13)	1.406(15)	1.397(15)	1.163(16)		174.7(12)	118.8(10)	179.0(14)	Monodentate	81
				1.434(18)	1.161(19)			121.1(10)	178.3(15)		
[Ru{C(CN)$_3$}(η-C$_5$H$_5$)-(PPh$_3$)$_2$]	2.071(6)	1.135(10)	1.391(12)	1.416(13)	1.127(12)		174.8(8)	117.2(8)	178.3(10)	Monodentate	82
				1.406(13)	1.149(14)			124.3(7)	177.9(13)		
[Fe{C(CN)$_3$}TTP]	2.317(3)	1.144(4)	1.403(3)	1.403(3)	1.144(4)	2.317(3)	174.0(3)	116.9(2)	174.0(3)	Bidentate	83
				1.423(6)	1.152(6)			125.9(4)	179.1(4)		
[Rh$_2${C(CN)$_3$}(form)$_4$]	2.07(3)	1.10(2)	1.55(4)	1.47(5)	1.12(3)		180	120(6)	133(7)	Monodentate	84

[a] The compound contains differently bonded C(CN)$_3$ groups; further data are in the subsequent row.

TABLE V Bond lengths (Å) and angles (°) of dicyanamide in various compounds

Compound	$M-N$	$N\equiv C$	$C-N$	$N-C$	$C\equiv N$	$(N-M)$	$-NCN$	CNC	(NCN)	*Bonding mode*	*Ref.*
$Li[N(CN)_2]$ 2MeCN	1.980(6)	1.139(5)	1.317(5)				175.2(4)	119.2(5)		Bidentate	85
$NaCs_2[N(CN)_2]_3$		1.153(3)	1.316(3)				172.7(3)	119.6(3)		Ionic	86
$Cs[N(CN)_2]$		1.18(2)	1.26(2)	1.31(2)	1.13(2)		172(2)	124(2)	173(2)	Ionic	28
$Ag[N(CN)_2]$ orthorhombic	2.14(2)	1.17(3)	1.28(3)	1.29(3)	1.16(3)	2.08(2)	172(3)	123(2)	170(2)	Bidentate	87
$Ag[N(CN)_2]$ trigonal	2.11(1)	1.15(1)	1.29(1)				170(2)	127(2)			88
κ-(BEDT-TTF)$_2[Cu\{N(CN)_2]Br$	1.963(7)	1.166(11)	1.306(11)	1.304(11)	1.156(11)	1.941(8)	174.2(9)	124.8(8)	170.5(9)	Bidentate	89
$Me_2Tl\{N(CN)_2\}$	2.60(4)	1.19(5)	1.31(5)	1.26(4)	1.18(4)	2.79(4) 2.81(4) 2.90(3)	172.0(44)	120.4(30)	171.4(43)	Tetradentate	51
$Me_3Sn\{N(CN)_2\}$	2.338(9)	1.109(14)	1.288(14)	1.237(15)	1.123(13)	2.333(9)	172.1(12)	129.6(11)	174.3(13)	Bidentate	90
$Me_2Sn\{N(CN)_2\}_2$	2.289(6)	1.138(9)	1.281(10)	1.297(8)	1.125(7)	2.289(5)	171.8(7)	124.2(8)	172.8(8)	Bidentate	90
$[Cu\{N(CN)_2\}(phen)_2]C(CN)_3$	1.982(4)	1.126(6)	1.282(7)	1.282(6)	1.1233(6)		172.8(5)	128.2(4)	172.6(5)	Monodentate	71
$[Cu\{N(CN)_2\}(mcoe)(bpy)]$	2.188(4)	1.133(6)	1.291(7)	1.294(7)	1.119(6)		172.8(5)	122.1(5)	172.9(5)	Monodentate	91
$[Cu\{N(CN)_2\}_2(phen)_2]$	2.365(3)	1.098(4)	1.324(5)	1.287(5)	1.091(5)		172.0(5)	120.6(4)	169.0(5)	Monodentate	68
$[Ni\{N(CN)_2\}_2(5\text{-meiz})_2]$	2.102(2)	1.144(3)	1.313(3)	1.313(3)	1.144(3)	2.102(2)	175.0(2)	117.8(3)	175.0(2)	Bidentate	69
$[Ni\{N(CN)_2\}_2(5\text{-meiz})_4]$	2.114(2)	1.140(3)	1.304(4)	1.291(3)	1.127(3)		172.6(3)	122.0(3)	172.8(3)	Monodentate	70
	2.120(2)	1.135(3)	1.305(3)	1.294(3)	1.141(3)		175.3(3)	120.6(3)	173.5(3)		
$[Re\{N(CN)_2\}(CO)_4]$	2.133(15)	1.136(24)	1.314(28)	1.197(33)	1.217(34)		173.0(20)	122.1(20)	174.8(24)	Monodentate	81
$[Ph_4P]_2[Co\{N(CN)_2\}_4]$	2.091(3)	1.152(4)	1.297(5)	1.311(5)	1.147(5)		172.0(3)	1.224(3)	173.4(4)	Monodentate	73
	2.177(3)	1.152(4)	1.311(4)	1.302(4)	1.154(4)	2.165(3)	173.2(3)	120.8(3)	172.9(3)	Bidentate	

In complexes with heterocyclic ligands of the pyridine type[37] the energies of the transitions $^3T_{2g} \leftarrow ^3A_{2g}$ indicate that the ligand field parameters of the present pseudohalides have the order Dq{C(CN)$_3$} > Dq{N(CN)$_2$}. It was ascertained that in the spectrochemical series the ions [C(CN)$_3$]$^-$ and [N(CN)$_2$]$^-$ are similar to the [NCS]$^-$ ligand. According to the calculated values of β the nephelauxetic effect of [C(CN)$_3$]$^-$ is weaker than that of [N(CN)$_2$]$^-$ which is nephelauxetically near to [NCO]$^-$. Dq values of both anionic ligands with decreasing denticity, for instance in the series [Ni{C(CN)$_3$}$_2$]–[Ni{C(CN)$_3$}$_2$(py)$_2$]–[Ni{C(CN)$_3$}$_2$(py)$_4$], increase and differences between Dq arise. For complexes with α-substituted pyridines and quinolines the Dq values are visibly lower than those of complexes with other pyridines as a consequence of steric hindrance of α-substituents. The d–d-spectra of Ni(II) complexes with 3- and 4-cyanopyridines[46] confirm the position of both pseudohalides in the spectrochemical series which follows from the spectra of pyridine complexes. The same is valid for complexes with pyrazole homologues.[21]

On the basis of the d–d-spectra one can divide Co(II) complexes into two categories. The first includes the compounds β-[Co{N(CN)$_2$}$_2$], [Co,Zn{N(CN)$_2$}$_2$],[40] the complex anion [Co{N(CN)$_2$}$_4$]$^{2-}$,[42] mixed complex anions [Co{N(CN)$_2$}$_2$(NCY)$_2$]$^{2-}$ and [Co{N(CN)$_2$}(NCY)$_3$]$^{2-}$ (Y = O, S),[53] [CoX$_2$L$_2$] (X = N(CN)$_2$, C(CN)$_3$; L = biz, 2-meiz, 4-meiz),[49,58] [Co{C(CN)$_3$}$_2$(biz)$_2$],[48] as well as the β-forms of the complexes [Co{C(CN)$_3$}$_2$(2-meiz)$_2$] and [Co{C(CN)$_3$}$_2$(4-meiz)$_2$].[49] In the visible region, one strong band centred around 1.70 μm^{-1} is mostly accompanied by absorptions at higher or lower wavenumbers. In the NIR region a further band appears at about 0.90 μm^{-1} which is also connected with supplementary absorptions. These bands, which prove the tetrahedral environment of the central Co(II) atom, are assigned to the transitions $^4T_1(P) \leftarrow ^4A_2$ and $^4T_1(F) \leftarrow ^4A_2$, respectively. Accompanying absorptions are connected with spin-forbidden transitions into doublet states or with spin–orbit coupling. Results for tetrakis(dicyanamido)cobalt(II) anions[42,53] allow one to verify the position of [N(CN)$_2$]$^-$ in the spectrochemical series Dq{N(CN)$_2$} $\approx$ Dq(NCS) and refer to a relatively strong nephelauxetic effect.

All remaining Co(II) complexes listed in Table II belong to the second category. In the visible region their spectra exhibit a band at about 2.2 μm^{-1} which is mostly split on the side of lower wavenumbers, and in the NIR region a band around 1.0 μm^{-1}. These bands, which indicate an octahedral configuration of the complexes, are assigned to the transitions $^4T_{1g}(P) \leftarrow ^4T_{1g}(F)$ and $^4T_{2g} \leftarrow ^4T_{1g}(F)$, respectively. The lateral absorptions on the first band may have different origins. Most are spin-forbidden transitions which borrow intensity from the allowed transitions. In these compounds as well $[C(CN)_3]^-$ is manifested as a ligand with a stronger ligand field, but one cannot observe any marked influence due to the type of neutral ligand or their steric properties. The ligand field parameters Dq and B are considerably greater than those estimated for the tetrahedral systems. In the case of dicyanamide–2-methyl- and 2-ethylbenzimidazole complexes the NIR band shows splitting in the region of $0.15\,\mu m^{-1}$ which indicates certain tetragonal distortion of the coordination geometry allowing two near IR transitions.[48,58]

Electronic d–d spectra of Cu(II) compounds in the visible range exhibit mostly one broad band which has often on the low-wavenumber side, and sometimes also on the high-wavenumber side, a more or less developed shoulder. On the basis of the position of this band, as well as from the position of the shoulders and their separation from the main band, stereochemical relations can be deduced. Using these criteria, tricyanomethanide and dicyanamide complexes of Cu(II) can be divided in four groups (Table VI) which represent different coordination polyhedra.

In the first group, just as for $[Cu\{C(CN)_3\}_2]$, the structure of which was solved crystallographically,[67] a broad band is situated at the lower limit of the wavenumber range. The other compounds of this group exhibit mostly on the low-wavenumber side a more or less developed shoulder, and sometimes

TABLE VI Survey of d–d-spectra of tricyanomethanido and dicyanamido copper(II) compounds

Approximate ranges of the d–d absorbtions (μm)	*Coordination geometry*	*Compound*
1.1–1.40sh[a] 1.35–1.8	Tetragonal bipyramidal	$[Cu\{C(CN)_3\}_2]$, $[Cu\{N(CN)_2\}_2]$, $[Me_4N]_2[Cu\{N(CN)_2\}_4]$, $[Cu\{C(CN)_3\}_2L_2]$, (L = 4-pic, 2-,4-etpy, 2,3-lut, quin, 3-, 4-CN-py, mpz, dmpz, tmpz, 4-NO_2-pz, biz, 2-mebiz, 1-meiz) $[Cu\{N(CN)_2\}_2L_2]$ (L = py, 2-, 4-pic, 2-, 4-etpy, 3,4-lut, quin, 2-, 3-, 4-ampy, 3-, 4-CN-py, 2-am-5-nipy, pz, mpz, dmpz, tmpz, inz, biz, 2-mebiz, 2-etbiz, $[Cu\{N(CN)_2\}_2(en)_2]$, $[Cu\{C(CN)_3\}(pz)_4][C(CN)_3]$
Around 1.3	*Cis*-distorted octahedral	$[Cu\{N(CN)_2\}_2(bpy)_2]$, $[Cu\{N(CN)_2\}_2(phen)_2]$
Close above 1.45 1.6–1.7sh	Rhombic-octahedral or square pyramidal	α-, β-$[Cu\{C(CN)_3\}_2(pz)_2]$
1.1–1.3	Pseudotetrahedral	$[Cu,Zn\{N(CN)_2\}_2]$, $[Ph_4As]_2[Cu\{N(CN)_2\}_4]$, $[Me_4N]_2[Cu\{N(CN)_2\}_4]$ (in solution)

[a] In the case of some compounds an additional shoulder between *ca.* 0.85–0.90 μm was observed (see Table II).
[b] Five-coordination can also be admitted.

two shoulders. To all these complexes one can ascribe a tetragonal-bipyramidal configuration around the Cu(II) atom with a variable degree of axial distortion. While the denticity of pseudohalides is lower than in $[Cu\{C(CN)_3\}_2]$ and nitrogen ligands with relatively strong ligand fields are present, the shift of d–d band maxima to higher energy is reasonable.

Positions of the d–d bands which can be assigned to transitions $^2E_g \leftarrow {}^2B_{1g}$ and $^2B_{2g} \leftarrow {}^2B_{1g}$ in the case of complexes with alkylpyridines, do not depend on the character of the neutral ligand, its basicity and steric properties, nor on the field of the present pseudohalides.[44] On the other hand, in pyrazole complexes the steric influence of methylpyrazoles and the spectrochemical effects of the pseudohalides are readily apparent.[21] Dicyanamide complexes with aminopyridines show maxima at the upper range of the spectra, probably caused by the strong positive inductive effect of the neutral ligands.[45] Shoulders at lower wavenumbers evidently belong to the $^2A_{1g} \leftarrow {}^2B_{1g}$ transition and their positions directly depend on the degree of the tetragonal distortion of the complex.[94] The electronic spectra of only a small number of Cu(II) complexes indicate another stereochemical arrangement: distorted *cis*-octahedral, five-coordinated and pseudo-tetrahedral.

5.2 Magnetic Properties

Magnetic susceptibilities of many tricyanomethanide and dicyanamide compounds of Cu(II), Ni(II) and Co(II) have been measured between *ca.* 300 and 4.2 K or at lower temperatures.[13–16,20,47,48,50,54,57,58,66] The χ_M values were fitted to the Curie–Weiss relation and the $\chi_M T$ or μ_{eff} *vs.* T functions explained in terms of exchange interaction between paramagnetic Cu(II) centres.

Kurmoo and Kepert[13] reported the results of an extensive study of magnetic properties of the compounds $[M\{N(CN)_2\}_2]$, where M is Cu, Ni, Co(α-form). Simultaneously, a second research group[14,15] reported the magnetic properties of the same compounds, as well as those of β-$[Co\{N(CN)_2\}_2]$. Magnetic susceptibilities for $[Cu\{N(CN)_2\}_2]$ are indicative of very weak antiferromagnetic coupling. The nickel(II) and cobalt(II) dicyanamides exhibit ferromagnetism and long-range ordering occurs ($T_c = 9$ and 21 K). These compounds are characterized by hysteresis loops, remnant magnetization and other attributes of hard magnets. Differences in magnetism within the given group of dicyanamides are found to depend strongly on M–N coordination distances and the degree of structural distortion. Magnetic properties of β-$[Cu\{N(CN)_2\}_2]$ are indicative of antiferromagnetic coupling and a magnetic phase change occurs at *ca.* 9 K.[15]

Hysteresis in magnetization was also ascertained. The nature of the ordered state is a spin-canted antiferromagnet.

Pseudohalide complexes with neutral ligands exhibit three kinds of the $\chi_M T$ *vs.* T dependence.[17] The first[20,47,54,57,66] is accounted for by both ferromagnetic and antiferromagnetic interactions, which are mediated by σ- and π-orbitals of the pseudohalide bridges. Even when the interaction of each kind is considerable, they are of opposite sign and, therefore, their influence on temperature-dependent magnetic behaviour is only slight. However, at lowest temperatures the magnetic systems indicate long-range ordering, ferromagnetic in character, which drastically changes the $\chi_M T$ *vs.* T plots. These functions exhibit maxima, after which a rapid fall of $\chi_M T$ values is indicative of intermolecular antiferromagnetic coupling between the polymeric or dimeric species present.

The second type of the $\chi_M T$ *vs.* T dependence[48,58,66] indicates that antiferromagnetic coupling is present in the respective compounds and at very low temperatures is strengthened by long-range magnetic ordering. It is worth mentioning the considerably different magnetic properties of the linkage isomers α- and β-[Cu{N(CN)$_2$}(iz)$_2$], which show distinct antiferromagnetic coupling and at lowest temperatures diverse long-range ordering, antiferromagnetic in the latter but ferromagnetic in the former.

The third type of the μ_{eff} T function[57,66] is explained by antiferromagnetic as well as ferromagnetic couplings, which are for the major part cancelled in such a manner that low, temperature independent μ_{eff} values result. Only at lowest temperatures do indications of increasing exchange interaction appear. The temperature-dependent magnetic properties of the pseudohalide complexes, mostly resulting from simultaneous ferro- and antiferromagnetic interactions, were discussed[17] in general on the basis of the theory given by Kahn *et al.*[97]

5.3 ESR Spectra

ESR spectra were recorded for the most of Cu(II) complexes in form of polycrystalline samples in the X-band range at room temperature and sometimes at low temperatures (4.2–193 K). Parameters obtained are listed in Table VII. Cu(II) complexes show ESR spectra of orthorhombic, axial, isotropic or almost isotropic type; some pseudo-isotropic spectra are substantially axial without resolved $g_{\parallel}$ values. All lines are of normal shape, which means that the intensities of the peaks in the weaker field (at $g_{\parallel}$) are lower than in the stronger field (at $g_{\perp}$ or g_1).

TABLE VII Parameters of ESR spectra for $[Cu\{N(CN)_2\}_2L_2]$ and $[Cu\{C(CN)_3\}_2L_2]$ complexes

Compound	*Type of spectrum*[a]	g_1 *or* $g_\perp$	g_2 *or* g_0[b]	g_3 *or* $g_\parallel$	g[c]	G[d]	*Ref.*
$[Cu\{N(CN)_2\}_2(py)_2]$	A	2.084		2.238	2.137	2.83	44
$[Cu\{N(CN)_2\}_2(2\text{-}pic)_2]$	P	2.064		[e]			44
$[Cu\{N(CN)_2\}_2(4\text{-}pic)_2]$	P		2.12				54
$[Cu\{C(CN)_3\}_2(4\text{-}pic)_2]$[f]	O	2.034	2.103	2.224	2.122	3.27	54
$[Cu\{N(CN)_2\}_2(3,4\text{-}lut)_2]$	A	2.050		2.205	2.103	4.10	44
$[Cu\{C(CN)_3\}_2(3,4\text{-}lut)_2]$	O	2.042	2.084	2.234	2.122	3.71	44
$[Cu\{N(CN)_2\}_2(2\text{-}etpy)_2]$	A	2.045		2.186	2.093	4.13	44
$[Cu\{C(CN)_3\}_2(2\text{-}etpy)_2]$	A	2.057		2.260	2.127	4.56	44
$[Cu\{N(CN)_2\}_2(4\text{-}etpy)_2]$	A	2.049		2.303	2.137	6.18	44
$[Cu\{C(CN)_3\}_2(4\text{-}etpy)_2]$	O	2.038	2.072	2.289	2.137	5.26	44
$[Cu\{N(CN)_2\}_2(quin)_2]$	P		2.08				44
$[Cu\{C(CN)_3\}_2(quin)_2]$	A	2.058		2.240	2.120	4.14	44
$[Cu\{C(CN)_3\}_2(3\text{-}CN\text{-}py)_2]$	O	2.051	2.070	2.271	2.133	4.48	44
$[Cu\{N(CN)_2\}_2(3\text{-}CN\text{-}py)_2]$	A	2.073		2.268	2.140	3.67	46
$[Cu\{C(CN)_3\}_2(4\text{-}CN\text{-}py)_2]$	A	2.069		2.269	2.138	3.90	46
$[Cu\{N(CN)_2\}_2(4\text{-}CN\text{-}py)_2]$	I		2.12				46
$[Cu\{N(CN)_2\}_2(pz)_2]$	A	2.082		2.250	2.139	3.05	56
$[Cu\{C(CN)_3\}_2(pz)_4]$	P		2.06				47
$[Cu\{C(CN)_3\}_2(pz)_3]$	P		2.08				47
α-$[Cu\{C(CN)_3\}_2(pz)_2]$	O	2.043	2.119	2.280	2.150		47
β-$[Cu\{C(CN)_3\}_2(pz)_2]$	O	2.044	2.117	2.302	2.157	3.79	47
$[Cu\{N(CN)_2\}_2(mpz)_2]$	P	2.040		[e]			21
$[Cu\{C(CN)_3\}_2(mpz)_2]$	A	2.028		2.276	2.114	9.86	21
$[Cu\{N(CN)_2\}_2(dmpz)_2]$	A	2.048		2.283	2.129	5.90	21
$[Cu\{C(CN)_3\}_2(dmpz)_2]$	I		2.12				21
$[Cu\{N(CN)_2\}_2(tmpz)_2]$	A	2.07		2.27	2.14	3.86	57
$[Cu\{C(CN)_3\}_2(tmpz)_2]$	A	2.09		2.34	2.18	3.78	57
$[Cu\{N(CN)_2\}_2(inz)_2]$	A	2.046		2.276	2.125	6.00	21
$[Cu\{C(CN)_3\}_2(biz)_2]$	A	2.064		2.18	2.10	2.81	48
$[Cu\{C(CN)_3\}_2(2\text{-}mebiz)_2]$	A	2.080		2.259	2.141	3.24	48
α-$[Cu\{N(CN)_2\}_2(iz)_2]$	A	2.082		2.232	2.132	2.83	66
β-$[Cu\{N(CN)_2\}_2(iz)_2]$	A	2.072		2.237	2.128	3.29	66
$[Cu\{C(CN)_3\}_2(2\text{-}meiz)_2]$	O	2.056	2.09	2.273	2.142	3.74	64
$[Cu\{C(CN)_3\}_2(4\text{-}meiz)_4]$	A	2.041		2.286	2.126	6.98	64
$[Cu\{N(CN)_2\}_2(2\text{-}ampy)_2]$	A	2.055		2.267		4.86	45
$[Cu\{N(CN)_2\}_2(3\text{-}ampy)_2]$	A	2.076		2.258		3.39	45
$[Cu\{N(CN)_2\}_2(4\text{-}ampy)_2]$	A	2.024		2.251		10.5	45
$[Cu\{N(CN)_2\}_2(2\text{-}am\text{-}5\text{-}nipy)_2]$	A	2.079		[e]			45
$[Cu\{N(CN)_2\}_2(biz)_2]$	A	2.050		[e]			58
$[Cu\{N(CN)_2\}_2(2\text{-}mebiz)_2]$	A	2.063		2.296	2.144	4.70	58
$[Cu\{N(CN)_2\}_2(2\text{-}etbiz)_2]$	A	2.059		2.282	2.136	4.78	58
$[Cu\{C(CN)_3\}_2(2\text{-}meiz)_2]$	O	2.056	2.09	2.273	2.142	3.74	64
$[Cu\{C(CN)_3\}_2(4\text{-}meiz)_4]$	A	2.041		2.286	2.126	6.98	64
$[Cu\{N(CN)_2\}_2(phen)_2]$	A	2.061		2.478	2.209	7.84	76

[a] I – isotropic, P – pseudoisotropic, A – axial, O – orthorhombic. [b] Determined in the inflection point of the derivative curve. [c] Calculated according to the relation $g = [(1/3)(g_\parallel^2 + 2g_\perp^2)]^{1/2}$ or $g = [(1/3)(g_1^2 + g_2^2 + g_3^2)]^{1/2}$. [d] Calculated according to the relation $G = (g_\parallel - 2)/(g_\perp - 2)$ or $G = (g_3 - 2)/[(1/2)(g_1 + g_2) - 2]$. [e] The value is not resolved. [f] The low-temperature spectrum.

The values $g_\perp$ or g_1, in the region of about 2.02–2.08, and the values of $g_\parallel(g_3)$, in the range 2.18–2.34, correspond with those ascertained for complexes of Cu(II) with elongated tetragonal or orthorhombic symmetry. Complexes with G parameters between 3.5 and 5.0 do not have g factors markedly influenced by exchange coupling. Therefore they correspond with true molecular g factors. The low g values [$g_\perp$ or $1/2(g_1+g_2)$] higher than 2.04 indicate the $d_{x^2-y^2}$ ground state of the Cu(II) central atom.

A considerable number of complexes have crystal g values outside the given region; they do not reflect exactly the local symmetry of the Cu(II) atom. The most important reason for this is exchange coupling operating through pseudohalide bridges between magnetically non-equivalent Cu(II) atoms. For some of these compounds exchange coupling was ascertained magnetochemically (see Section 5.2). In some cases also the anisotropy of the $g_\perp$ factor which is unresolved under the given measurement conditions is a possible reason for a high G value. One-line spectra near to isotropic ones are most likely conditioned also by exchange interaction between misaligned molecules in the unit cell.[94,98] If the room-temperature spectra are unresolved, measurements at low temperature resolve 2g or 3g sometimes.[54,57]

The isomers α- and β-[Cu{C(CN)$_3$}$_2$(pz)$_2$] exhibit orthorhombic ESR spectra with similar g values especially for both perpendicular values (g_1, g_2).[47] ESR spectra of the linkage isomers α- and β-[Cu{N(CN)$_2$}$_2$(iz)$_2$] are of axial type.[8] The pertinent g values are similar and the calculated G parameters suggest that the molecular g values are modified as a result of cooperative effects.[66] [Cu{C(CN)$_3$}$_2$(4-meiz)$_4$] shows an axial ESR spectrum with clearly resolved hyperfine splitting in the $g_\parallel$ part.[64] ESR spectra of the compounds [Cu{N(CN)$_2$}$_2$(4-pic)$_2$], [Cu{C(CN)$_3$}$_2$(4-pic)$_2$], [Cu{C(CN)$_3$}$_2$(pz)$_3$], [Cu{C(CN)$_3$}$_2$(biz)$_2$], [Cu{C(CN)$_3$}$_2$(2-mebiz)$_2$] exhibit at lower temperature at 150–160 mT a weak signal which corresponds with the transition $\Delta M_s = 2$ in a triplet state diagnostic of exchange coupling between Cu(II) atoms.[47,48,54]

6 VIBRATIONAL SPECTRA

6.1 Stretching CN Vibrations in IR Spectra

In the middle IR region the CN stretching vibration is of diagnostic value for the bonding mode of the pseudohalide ligands. On the basis of ν(CN) values the bonding modes of the pseudohalide in the complexes under study were estimated as listed in Table VIII. The ν(CN) vibration causes strong bands centered in two absorption regions. The low-frequency region is usually broader than the high-frequency one and the corresponding bands have visibly lower intensity than the higher-frequency bands. For compounds [M{N(CN)$_2$}$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn),[40] as well as for some anionic dicyanamido complexes,[43,53] the high-frequency bands were assigned to ν_{as}(CN) and the low-frequency one to ν_s(CN). However, these assignments

TABLE VIII Bonding mode of anionic ligands in tricyanomethanide and dicyanamide compounds of Cu(II), Ni(II), Co(II) on the basis of IR spectroscopy

Approximate region $\nu(CN)$ (cm^{-1})	*Bonding mode*	*Compound*
C(CN)$_3$ group		
2230–2215 2185–2165^{a}	Monodentate	$[M\{C(CN)_3\}_2(py)_4]$ (M = Ni, Co), $[Co\{C(CN)_3\}_2L_4]$ (L = 2-meiz, 4-meiz), $[Cu\{C(CN)_3\}_2(HMPA)_4]$, $[Co\{C(CN)_3\} \cdot (NO)_2(PPh_3)]$, $[Co\{C(CN)_3\} \cdot (NO)_2\{Pcy_3\}]$, $[Ni\{C(CN)_3\} \cdot (NO)\{PCy_3\}_2]$, $[Ni\{C(CN)_3\} \cdot (NO)(C_2H_4)\{PCy_3\}_2]$
2260–2240 2210–2165^{a}	Bidentate	$[Cu\{C(CN)_3\}_2L_2]$ (L = py, 4-pic, 2-etpy, 4-etpy, 3,4-lut, quin, 3-CN-py, 4-CN-py, pz, dmpz, tmpz, iz, 2-meiz, 4-meiz) $[Ni\{C(CN)_3\}_2L_2]$ (L = py, 2-pic, 2,4-lut, 3-CN-py, 4-CN-py, pz, tmpz, HMPA), $[Co\{C(CN)_3\}_2L_2]$ (L = py, 2-pic, 2,4-lut, *i*-quin, iz, biz, HMPA), α-$[Co\{C(CN)_3\}_2(4\text{-meiz})_2]$, $[Ni\{C(CN)_3\}_2L_4]$ (L = quin, *i*-quin), $[Ni\{C(CN)_3\} \cdot (NO)\{PCy_3\}_2]$
2275–2270 2225–2205^{a}	Tridentate	$[Cu\{C(CN)_3\}_2]$, $[Ni\{C(CN)_3\}_2]$, $[Co\{C(CN)_3\}_2]$, $[Co\{C(CN)_3\}(NO)]$
N(CN)$_2$ group		
2240–2210 2190–2160	Monodentate	$[Ph_4As]_2[Cu\{N(CN)_2\}_4]$, $[Me_4N]_2[Cu\{N(CN)_2\}_4]$, $[Ph_3MeAs]_2[Co\{N(CN)_2\}_4]$, (in solution) $K_2[Co\{N(CN)_2\}_2(NCS)_2]$, $[Ph_4P]_2[Co\{N(CN)_2\}_2(NCY)_2]$, (Y = O, S) $[Cu\{N(CN)_2\}_2(2\text{-ampy})_2]$, $[M\{N(CN)_2\}_2L_2]$ (L = Cu, Ni, Co; L = en, bpy, phen), $[Co\{N(CN)_2\}_2(C_6H_5CH_2NC)_2]$ $[Co\{N(CN)_2\}_2(2\text{-meiz})_2]$, $[Co\{N(CN)_2\}_2(4\text{-meiz})_2]$, $[Co\{N(CN)_2\}_2(biz)_2]$
2260–2240^{b} 2210–2180^{c}	Bidentate	$[Ph_4P][Ni\{N(CN)_2\}_3]$ $[Ph_4As]\,[Ni\{N(CN)_2\}_3]$ $[Ph_3MeAs][Co\{N(CN)_2\}_3]$ $[Ph_4P]_2[Ni\{N(CN)_2\}_2(NCS)_2]$ $[Ph_4As]_2[Ni\{N(CN)_2\}_2(NCS)_2]$ $[M\{N(CN)_2\}_2L_2]$ (M = Cu, Ni, Co; L = py, 2-pic, 4-pic, 2-am-5-nipy, pz, DMSO), $[Cu\{N(CN)_2\}_2L_2]$ (L = 2-etpy, 4-etpy, 3,4-lut, quin, 3-ampy, 4-ampy, 3-CN-py, 4-CN-py, mpz, dmpz, tmpz, inz, 2-mebiz) $[Ni\{N(CN)_2\}_2L_2]$ (L = 2,4-lut, 2-ampy, 3-ampy, 4-ampy, 3-CN-py, 4-CN-py, tmpz, iz, 1-meiz, 2-mebiz, 2-etbiz, OMNA) $[Co\{N(CN)_2\}_2L_2]$ (L = 2,3-lut, quin, 1-meiz, OMNA) $[Ni\{N(CN)_2\}_2L_4$ (L = quin, *i* = quin)

TABLE VIII (*Continued*)

Approximate region (CN) (cm^{-1})	*Bonding mode*	*Compound*
2260–2240	Bidentate and	$[Me_4N]_2\{Cu\{N(CN)_2\}_4]$
2200–2170	Monodentate	$[Ph_3MeAs]_2\{Co\{N(CN)_2\}_4]$
2260–2250	Tridentate and	$[Ni\{N(CN)_2\}_2]$
2210	Monodentate	α-$[Co\{N(CN)_2\}_2]$
2280	Tridentate and	$K[Ni_2\{N(CN)_2\}_5]$
~2210, ~2180	Monodentate	
~2210, ~2180	Monodentate	

[a] Normally two or three bands occur. [b] In some cases two bands occur. [c] In some cases a further band between 2170 and 2140 cm^{-1} occurs.

are at variance with results of polarized Raman spectra.[99] The number of ν_{as}(CN) bands shows distinctly that these vibrations are conditioned not only by the point symmetry of the pseudohalide ligand but also by its position in the crystal structure leading to the correlated field splitting.

From Table VIII it becomes clear that the usual bonding mode of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions is the bidentate function, which shows the considerable ability of these ligands to bridging functions. Rather rarely these ligands function as monodentates, tridentates or in a mixed form (mono- and tridentates). Reliable determination of the bonding mode only by IR spectroscopy is rather difficult. Besides the type of coordination (mono-, bi-, tridentate), the character of the more ionic or covalent nitrogen–metal bond, and in the case of more ionic interactions the mass of the vibrational system as well as polarization effects of the cations, strongly influences the CN stretching vibrations. Köhler thus reported discrepancies between bonding mode and generally expected frequencies.[37,40] In more recent papers,[48,49,58,65] values of ν(CN) vibrations are not consistent with these criteria. Discrepancies between the pseudohalide bonding mode and the ν(CN) frequency observed in these cases can be connected with the variability of C≡N bond lengths which do not show a distinct dependence on the bonding mode of the pseudohalide present (see Tables IV and V). It seems that only X-ray crystallography can give reliable information on the bonding mode of these pseudohalides.

6.2 Far IR Spectra

Far IR spectra can give further information on structure relations in tricyanomethanide and dicyanamide complexes. Table IX contains data for ν(M–N) stretching vibrations for pseudohalide compounds of Cu(II), Ni(II) and Co(II) recorded to 200 or 50 cm^{-1}. Values of ν(M–N) for metal tricyanomethanides[31] increase regularly from Co(II) to Cu(II) indicating the

TABLE IX Frequencies of the M–N (ligand) stretching vibration for pseudohalide complexes

Compound	$\nu(M{-}N)$ (cm^{-1})	*Ref.*
$[Cu\{C(CN)_3\}_2]$	292m, 272m	104
$[Ni\{C(CN)_3\}_2]$	311s, 280m, 260m	104
$[Co[C(CN)_3\}_2]$	302s, 266sh, 252m, br	104
$[Cu\{N(CN)_2\}_2]$	356m, 328s, 305m, 277s	104
$[Ni\{N(CN)_2\}_2]$	325ms, 305sh, 270m	40
α-$[Co\{N(CN)_2\}_2]$	316sh, 304s, 280s, 280sh	40
β-$[Co\{N(CN)_2\}_2]$	364ms, 308m, 290sh	40
$[Cu\{N(CN)_2\}_2(py)_2]$	304s, 286vs	44
$[Cu\{N(CN)_2\}_2(2\text{-pic})_2]$	322sh, 316m, 263m	44
$[Cu\{C(CN)_3\}_2(4\text{-pic})_2]$	267s, 212w	44
$[Cu\{N(CN)_2\}_2(4\text{-pic})_2]$	267s, 243w^a	44
$[Cu\{C(CN)_3\}_2(3,4\text{-lut})_2]$	271m, 227w	44
$[Cu\{N(CN)_2\}_2(3,4\text{-lut})_2]$	267m, 243w^a	44
$[Cu\{C(CN)_3\}_2(2\text{-etpy})_2]$	272m, 235m	44
$[Cu\{N(CN)_2\}_2(2\text{-etpy})_2]$	333w, 276w, 265w	44
$[Cu\{C(CN)_3\}_2(4\text{-etpy})_2]$	278w, 263s, 210sh	44
$[Cu\{N(CN)_2\}_2(4\text{-etpy})_2]$	350w, 312w, 274m, 263w	44
$[Cu\{C(CN)_3\}_2(quin)_2]$	286s, 239m	44
$[Cu\{N(CN)_2\}_2(quin)_2]$	322s, 263s	44
$[Cu\{N(CN)_2\}_2(2\text{-ampy})_2]^b$	332m, 273ms, 246m^a, 105w, 96sh	45
$[Cu\{N(CN)_2\}_2(3\text{-ampy})_2]^b$	299m, 260s, 233m, 91w	45
$[Cu\{N(CN)_2\}_2(4\text{-ampy})_2]^b$	290m, 265vw, 247w^a, 93w	45
$[Cu\{N(CN)_2\}_2(2\text{-am-5-nipy})_2]^b$	322m, 287m, 266m, 242ms^a, 89m	45
$[Ni\{N(CN)_2\}_2(2\text{-ampy})_2]^b$	260s,br, 253sh, 246sh	45
$[Ni\{N(CN)_2\}_2(3\text{-ampy})_2]^b$	271s,br, 255sh	45
$[Ni\{N(CN)_2\}_2(4\text{-ampy})_2]^b$	273s, 254sh	45
$[Ni\{N(CN)_2\}_2(2\text{-am-5-nipy})_2]^b$	286s, 280s, 245s^a, 230s	45
$[Co\{N(CN)_2\}_2(2\text{-am-5-nipy})_2]^b$	266s, 227sh	45
$[Cu\{C(CN)_3\}_2(3\text{-CN-py})_2]$	288w, 268mw, 248w	46
$[Ni\{C(CN)_3\}_2(3\text{-CN-py})_2]$	276s, 268s, 260s, 244vs	46
$[Cu\{N(CN)_2\}_2(3\text{-CN-py})_2]$	316s, 260s	46
$[Ni\{N(CN)_2\}_2(3\text{-CN-py})_2]$	276vs, 260s, 224s	46
$[Cu\{C(CN)_3\}_2(4\text{-CN-py})_2]$	292w, 252mw, 232mw	46
$[Ni\{C(CN)_3\}_2(4\text{-CN-py})_2]$	276s, 256s, 248s	46
$[Cu\{N(CN)_2\}_2(4\text{-CN-py})_2]$	304ms, 252s^a	46
$[Ni\{N(CN)_2\}_2(4\text{-CN-py})_2]$	272vs, 252vs^a, 236s	46
$[Cu\{C(CN)_3\}_2(pz)_4]$	278vs, 242w	47
$[Cu\{C(CN)_3\}_2(pz)_3]$	290sh, 286vs, 243mw	47
α-$[Cu\{C(CN)_3\}_2(pz)_2]$	292s, 229ms, 221ms	47
β-$[Cu\{C(CN)_3\}_2(pz)_2]$	291vs, 230sh, 221ms	47
$[Ni\{C(CN)_3\}_2(pz)_2]$	274s, 257s	21
$[Cu\{N(CN)_2\}_2(pz)_2]^b$	308sh, 298s, 105m	56
$[Ni\{N(CN)_2\}_2(pz)_2]^b$	268vs, 233s	21
$[Co\{N(CN)_2\}_2(pz)_2]$	256vs, 251vs, 246vs	21
$[Cu\{C(CN)_3\}_2(mpz)_2]$	293vs, 272ms,br^a	21
$[Cu\{N(CN)_2\}_2(mpz)_2]^b$	290vs, 281sh, 88ms	21
$[Cu\{C(CN)_3\}_2(dmpz)_2]^b$	308vs, 270sh, 253s, 93m	21
$[Cu\{N(CN)_2\}_2(dmpz)_2]$	326m, 307m, 286m, 244s	21
$[Cu\{C(CN)_3\}_2(tmpz)_2]^b$	302s, 284s^a, 265s, 94m^a	57
$[Cu\{N(CN)_2\}_2(tmpz)_2]^b$	292s,br, 247s, 94sh^a	57
$[Ni\{N(CN)_2\}_2(mpz)_2]$	274s, 257s	21
$[Cu\{N(CN)_2\}_2(inz)_2]$	288m,br, 265vs	21
$[Cu\{C(CN)_3)\}_2(4\text{-Cl-pz})_2]$	316m^a, 286m^a, 262w	55

TABLE IX (*Continued*)

Compound	$\nu(M{-}N)$ (cm^{-1})	*Ref.*
$[\mathrm{Cu\{C(CN)_3)\}_2(4\text{-}Br\text{-}pz)_2}]$	307mw, 263ms[a], 232w[a]	55
$[\mathrm{Ni\{C(CN)_3\}_2(4\text{-}Br\text{-}pz)_2}]$	299mw, 264m[a], 258sh[a], 231m[a]	55
$[\mathrm{Co\{C(CN)_3\}_2}]$	288w, 257w[a], 238m[a]	55
$[\mathrm{Cu\{N(CN)_2\}_2(4\text{-}Br\text{-}pz)_2}]$	303ms, 268s, 258s	55
$[\mathrm{Co\{N(CN)_2\}_2(iz)_2}]$	271m, 254w	49
$[\mathrm{Co\{C(CN)_3\}_2(iz)_2}]$	264m, 251m	49
$[\mathrm{Co\{N(CN)_2\}_2(2\text{-}meiz)_2}]$	427m, 385mw[a], 323mw, 316w, 278w[b], 257w[b]	49
α-$[\mathrm{Co\{C(CN)_3\}_2(2\text{-}meiz)_2}]$	271m[b], 251ms[b]	49
β-$[\mathrm{Co\{C(CN)_3\}_2(2\text{-}meiz)_2}]$	429s, 392mw[b], 385sh[b], 385sh[b], 319ms, 276m[b], 254ms[b]	49
$[\mathrm{Co\{N(CN)_2\}_2(4\text{-}meiz)_2}]$	391vw, 332vw, 263ms[a]	49
α-$[\mathrm{Co\{C(CN)_3\}_2(4\text{-}meiz)_2}]$	288m[b], 254m[b]	49
β-$[\mathrm{Co\{C(CN)_3\}_2(4\text{-}meiz)_2}]$	390vw, 328vw, 269ms[b], 264sh[b], 243ms	49
$[\mathrm{Cu\{C(CN)_3\}_2(biz)_2}]$	312ms, 303ms, 266m	48
$[\mathrm{Cu\{C(CN)_3\}_2(2\text{-}mebiz)_2}]$	315w, 292w, 283w, 255w	48
$[\mathrm{Ni\{C(CN)_3\}_2(biz)_2}]$	309m, 297ms, 257m	48
$[\mathrm{Ni\{C(CN)_3\}_2(2\text{-}mebiz)_2}]$	308m, 286m, 261m	48
$[\mathrm{Co\{C(CN)_3\}_2(biz)_2}]$	297m, 273sh	48
$[\mathrm{Co\{C(CN)_3\}_2(2\text{-}mebiz)_2}]$	304m, 280m, 249m	48
$[\mathrm{Co\{N(CN)_2\}_2(2\text{-}mebiz)_2}]$	268m, 243sh	48
$[\mathrm{Cu\{N(CN)_2\}_2(biz)_2}]$	320m, 287s	58
$[\mathrm{Cu\{N(CN)_2\}_2(2\text{-}mebiz)_2}]$	303m, 291m	58
$[\mathrm{Cu\{N(CN)_2\}_2(2\text{-}etbiz)_2}]$	359w, 314m, 305m[a], 272ms	58
$[\mathrm{Ni\{N(CN)_2\}_2(biz)_2}]$	301m, 267ms	58
$[\mathrm{Ni\{N(CN)_2\}_2(2\text{-}mebiz)_2}]$	300m, 287ms, 267ms	58
$[\mathrm{Ni\{N(CN)_2\}_2(2\text{-}etbiz)_2}]$	363w, 312w, 298m	58
$[\mathrm{Co\{N(CN)_2\}_2(biz)_2}]$	289m, 257sh	58
$[\mathrm{Co\{N(CN)_2\}_2(2\text{-}etbiz)_2}]$	362m, 290ms	58
$[\mathrm{Cu\{C(CN)_3\}_2(4\text{-}NO_2\text{-}pz)_2}]$	348m, 298s, 290sh, 272m, 263sh	65
$[\mathrm{Ni\{N(CN)_2\}_2(4\text{-}NO_2\text{-}pz)_2}]$	335vw, 293s, 247s	65
$[\mathrm{Cu\{N(CN)_2\}_2(1\text{-}meiz)_2}]$	295s, 280ms	50
$[\mathrm{Ni\{N(CN)_2\}_2(iz)_2}]$	284ms, 260sh, 246s	50
$[\mathrm{Ni\{N(CN)_2\}_2(1\text{-}meiz)_2}]$	286s, 257sh, 246s	50
$[\mathrm{Co\{N(CN)_2\}_2(1\text{-}meiz)_2}]$	260s, 250s, 235s, 224s	50
α-$[\mathrm{Cu\{N(CN)_2\}_2(iz)_2}]$	310sh, 295s, 260w	66
β-$[\mathrm{Cu\{N(CN)_2\}_2(iz)_2}]$	366m, 310sh, 295s, 260w	66
$[\mathrm{Cu\{N(CN)_2]_2(phen)_2}]$	310m, 287m, 247m	95

[a] An interference with a band of ligand L is possible. [b] The spectrum was measured to 50 cm^{-1}.

increase of bond strength with rising ligand field stabilization. For metal dicyanamides[40] two regions of ν(M–N) values were observed. In the case of β-isomers the bands above 300 cm^{-1}, compared with those of the α-isomers, are distinctly shifted to higher frequencies, apparently due to the tetrahedral structures.

In the compounds $[\mathrm{M\{N(CN)_2\}_2L_2}\}$ some ν(M–N) bands were found at frequencies considerably higher than 300 cm^{-1}, and following Köhler *et al.*[40] these bands were assigned to ν(M–N(amide)) vibrations. Therefore, dicyanamide bridges of the type (VII) were assumed, but without X-ray crystallographic corroboration.

For pseudohalide complexes with neutral ligands one often observes split ν(M–N) bands which indicate an asymmetry of the coordination polyhedron (especially for complexes of Cu(II)), as well as correlation effects of the crystal structures. Because the vibrations ν[M–N(nitrile)] and ν[M–N(L)] are energetically similar, mutual influence and mixing can be expected. This could be one of the reasons that we do not find any influence of the character of the neutral ligand on ν(M–N) as observed in analogous cyanate complexes of Cu(II).[101–103]

For about 15 complexes the FIR spectra were recorded to 50 cm^{-1}.[21,45,56,57] In the case of Cu(II) complexes in the region between 105 and 90 cm^{-1}, weak to medium intensity bands were observed, assigned to the Cu–N stretching vibration of the long, apical bonds with the pseudohalide in bridging function. Such bands for axial stretching vibrations were not observed for Ni(II) complexes because their distortion is much weaker than for Cu(II) complexes. FIR spectra of pseudotetrahedral Co(II) compounds sometimes contain four ν(Co–N) absorptions. Some of them appear at quite high wavenumbers (above 400 cm^{-1}).[49]

6.3 Raman Spectra

Besides IR spectra Civadze *et al.*[59] studied laser Raman spectra of K[N(CN)$_2$] and [M{N(CN)}$_2$(OMNA)$_2$] (M = Ni, Co) in the region between 4000 and 30 cm^{-1}. Depolarization of the Raman lines of [N(CN)$_2$]$^-$ gave precision to the assignment of frequencies in IR spectra. They showed that in contrast to the former assignment in the IR spectra the higher frequency component of the CN vibration has to be assigned to ν_s and the lower frequency component to ν_{as}(NCN). The increase of ν_s and ν_{as}(NCN) values in the IR as well as the Raman spectra of the complexes (2260–2160 cm^{-1}) in comparison with the [N(CN)$_2$]$^-$ ion indicates the formation of dicyanamide bridges. The intense Raman lines at about 260 cm^{-1} belong to M–N stretching vibrations.

Civadze and Köhler[99] measured Raman spectra of a series of metal dicyanamides [M{N(CN)$_2$}$_2$] (M = Mn, Fe, Co, Ni, Cu, Zn) as well as of pyridine complexes [M{N(CN)$_2$}$_2$(py)$_2$] (M = Mn, Co, Ni, Cu, Zn). According to the polarization results they assigned[59] the higher frequency lines to ν_s(CN) and the lower frequency ones to ν_{as}(CN). They discussed the characteristic changes of Raman line frequencies in terms of various parameters and compared the features of the Raman spectra in important regions with the IR spectra formerly measured. The main result of these studies is the confirmation of the existence of two different structural types of metal dicyanamides as well as the verification of the same coordination function of $N(CN)_2$ groups in the complexes $[M\{N(CN)_2\}_2(py)_2]$.

The same authors[100] investigated the Raman spectra of 3*d*-metal tricyanomethanides $[M\{C(CN)_3\}_2]$ as well as $[Ni\{C(CN)_3\}_2(py)_4]$, assigned observed lines and discussed characteristic variations of their position and intensity. The most important result is the assignment of the bands in the range of 2270–2252 to $\nu_s(CN)$ and those between 2215 and 2180 cm^{-1} to components of two-fold degenerate $\nu_d(CN)$ mode. Vibrations of both kinds are in comparison with $K[C(CN)_3]$ distinctly shifted to higher frequencies.

7 ESCA SPECTRA

Salyn *et al.*[105] recorded X-ray photoelectronic spectra of $K[C(CN)_3]$ and $Na[N(CN)_2]$ as well as of a series of tricyanomethanide and dicyanamide complexes in which on the basis of indirect structural results one can suppose different bonding modes or different functionality of the pseudohalide ligands. In almost all these complexes N1s binding energies in comparison with the free ligands are increased by 0.2–0.7 eV, caused by the partial transition of ionic charge of the ligand to the metal as a consequence of the formation of a coordination σ-bond. In the case of the compounds MX_2 ($M = Mn-Zn$, $X = C(CN)_3$, $N(CN)_2$) a distinctly higher relative increase of binding energy for N1s was established in dicyanamides compared to analogous tricyanomethanides. Therefore dicyanamide is apparently a stronger donor than tricyanomethanide.

For dicyanamides there was observed the same increase of the N1s (nitrile) binding energy as well as N1s (amide), in agreement with the donor abilities of N(nitrile) and N(amide). For the anionic complex $Ph_4P[Ni\{N(CN)_2\}_3]$, in which only the nitrile N atoms form coordination bonds, the electronic density of these atoms is markedly decreased and on the amide N atom somewhat increased. Observed reduction of electron densities in complexes $[M\{N(CN)_2\}_2(DMSO)_2]$ on both amide and nitrile nitrogens of $N(CN)_2$ ligands does not allow one to differentiate between the possible bonding types (VI) and (VII).

8 STRUCTURAL ASPECTS

The compounds $[M\{C(CN)_3\}_2]$ ($M = Cu$, Ni, Co)[67] are coordination polymers with tridentate bridging $C(CN)_3$ groups which form around the central

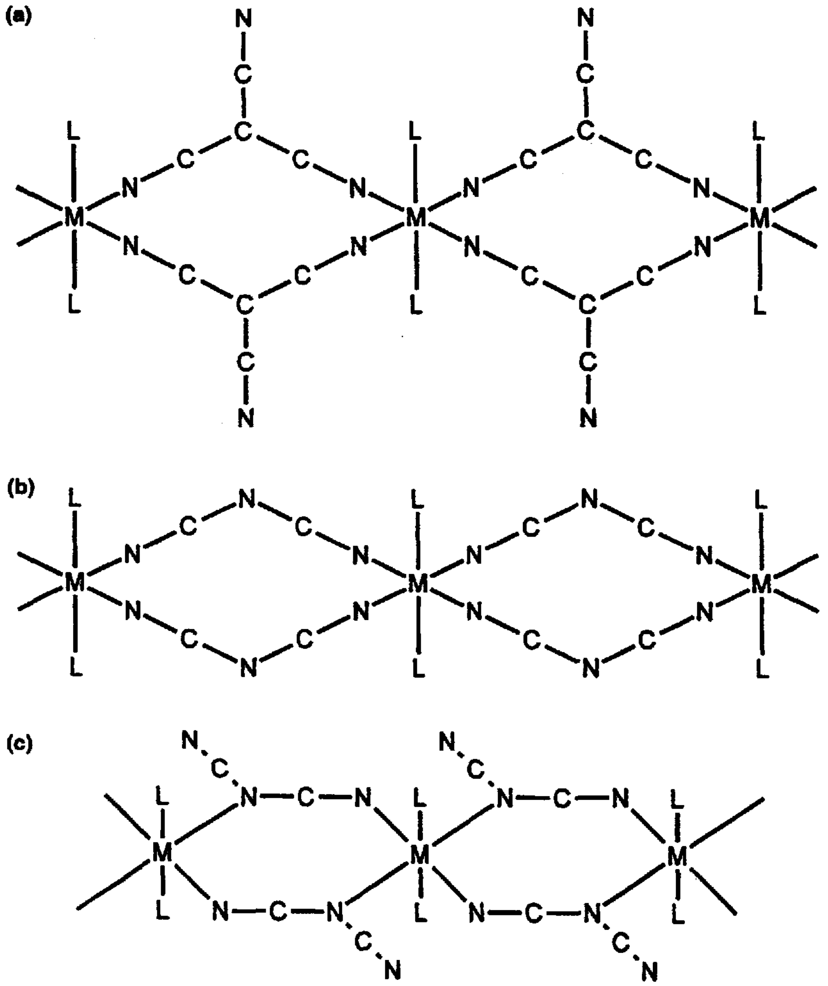
M atom a distorted octahedron of nitrogen atoms. Compounds $[M\{N(CN)_2\}_2]$ (M = Cu, Ni, Co – α-form)[13,14] also form polymeric structures with pseudo-octahedral arrangement of nitrogen atoms around the central M atom. In comparison to the copper(II) compounds, where Jahn–Teller or pseudo-Jahn–Teller effects operate,[96] for other metals much weaker distortion of the coordination polyhedron was observed. Another structure type is represented by β-$[Co\{N(CN)_2\}_2]$[15] in which bidentate bridging $N(CN)_2$ ligands realize *via* nitrile nitrogens tetrahedral coordination of Co(II). The existence of the Co(II) structural isomers is evidently allowed by small differences between the stabilization of Co(II) in tetrahedral or octahedral fields.

Only dicyanamide forms stable anionic complexes with Cu(II), Ni(II) and Co(II) ions. These complex anions have either a monomeric tetrahedral or a polymeric octahedral structure depending on the character of the central atom, conditions of their formation as well as of their state (solution or solid state). Complexes of Cu(II) are distorted.[40–43]

Tricyanomethanide and dicyanamide complexes of the given metals and neutral ligands are mainly of two types: $[MX_2L_2]$ and $[MX_2L_4]$ (X = $N(CN)_2$ and $C(CN)_3$). Only a few of these have a monomeric structure. This is connected with the monodentate function of pseudohalide ligands, given by the tendency of neutral ligands to occupy more coordination places or by their chelate properties.

To the category with a molecular structure belong the complexes $[M\{C(CN)_3\}_2(py)_4]$ (M = Co, Ni),[35] $[Ni\{N(CN)_2\}_2(5\text{-meiz})_4]$,[70] $[Cu\{C(CN)_3\}_2L_4]$ (L = 2-meiz, 4-meiz)[64] and $[Cu\{C(CN)_3\}_2(HMPA)_4]$.[37] Compounds $[M\{N(CN)_2\}_2L_2]$ (M = Cu, Ni, Co; L = en, bpy, phen)[60] and $[Cu\{C(CN)_3\}_2(phen)_2]$[68] have octahedral *cis*-configurations which in the case of Cu(II) is distorted. The complexes $[Co\{C(CN)_3\}_2L_2]$ (L = 2-meiz, β-form; 4-meiz, β-form; biz),[48,49] $[Co\{N(CN)_2\}_2L_2]$ (L = 2-meiz, 4-meiz, biz)[49,58] and $[Co\{N(CN)_2\}_2(C_6H_5CH_2NC)_2]$[6] show a tetrahedral structure.

$[MX_2L_2]$ complexes containing bidentate pseudohalide groups represent in all cases coordination polymers. One can suppose that $C(CN)_3$ or $N(CN)_2$ ligands are equatorially bonded through one nitrogen to the central M atom and form with a second nitrogen atom axial bonds to the M atom of an adjacent structural unit. This polymeric arrangement can be of the chain type (Scheme 3) evidenced by X-ray crystallography for $[Ni\{N(CN)_2\}_2(5\text{-meiz})_2]$[69] and α-$[Co\{C(CN)_3\}_2(2\text{-meiz})_2]$.[49] On the basis of cryomagnetic properties a chain structure was suggested for $[CuX_2(4\text{-pic})_2]$ (X = $C(CN)_3$, $N(CN)_2$),[54] $[Cu\{N(CN)_2\}_2(pz)_2]$,[56] and α- and β-$[Cu\{C(CN)_3\}_2(pz)_2]$,[47] as well as for α- and β-$[Cu\{N(CN)_2\}_2(iz)_2]$.[66]



SCHEME 3 Chain structures of the complexes $[M\{C(CN)_3\}_2L_2]$ (a) and $[M\{N(CN)_2\}_2L_2]$ (b, c).

On the contrary, for $[Cu\{C(CN)_3\}_2(2\text{-meiz})_2]$[64] a two-dimensional layer structure was crystallographically proven and in the case of $[CuX_2(tmpz)_2]$ ($X = C(CN)_3$, $N(CN)_2$),[57] magnetic properties suggest a three-dimensional network. In all polymeric arrangements, octahedral MN_6 or *trans*-MN_4O_2 chromophores are present depending on the type of neutral ligands. In the case of Cu(II) the octahedral geometry is distorted by axial elongation.

An important finding is that complexes with sterically bulky ligands, *e.g.*, α-substituted pyridines and quinolines[37,38,44] show a polymeric octahedral or pseudo-octahedral structure. The steric influence of these ligands causes a decrease of the 10Dq values for Ni(II) complexes. In the case of Cu(II) complexes it does not have a marked influence on the degree of axial distortion.[44] On the other hand analogous cyanato and thiocyanato complexes of Ni(II) or Co(II) are monomeric planar or tetrahedral and in copper(II) complexes the degree of bonding interaction in axial or equatorial directions visibly changes.[101,106–108]

Structure–bonding differences of similar character are also observable for pseudohalide complexes with methylpyrazoles which have steric effects. All isolated tricyanomethanide and dicyanamide complexes of Ni(II) and Cu(II) are octahedral or pseudo-octahedral and the steric interference reflects on the degree of axial interaction or ligand field strength and depends also on the kind of anionic ligand.[21,57]

In dicyanamide complexes of Ni(II) and Cu(II) with benzimidazoles steric effects of the neutral ligand dominate in comparison to their basicity, as revealed by decreasing 10Dq values in the order biz > 2-mebiz > 2-etbiz.[58] On the basis of the d–d-spectra $[Ni\{C(CN)_3\}_2(biz)_2]$ is supposed to possess a pseudo-octahedral configuration in which the Ni(II) atom forms four longer bonds with bridging $C(CN)_3$ groups and two shorter ones to benzimidazole.[48] The group of complexes Ni(II), Co(II)–$C(CN)_3$, $N(CN)_2$–2-mebiz, especially $[Co\{N(CN)_2\}_2(2\text{-mebiz})_2]$, show distorted octahedral structures. The other compounds are octahedral without regard to steric hindrance of the neutral ligands.[48] Analogously, $[Co\{N(CN)_2\}_2(2\text{-etbiz})_2]$ with a stronger steric effect of 2-etbiz, is distorted and six-coordinate.[58] All foregoing structural features and differences are most probably conditioned, first of all, with the ability of $C(CN)_3$ and $N(CN)_2$ ligands to form strong bridges and adapt to steric effects of other ligands.

Compounds $[NiX_2L_4]$ (L = quin, *i*-quin), $[Co(C(CN)_3\}_2(i\text{-quin})_4]$ and $[Co\{N(CN)_2\}_2(quin)_4]$ show also polymeric octahedral structures[37,39] while they contain bidentate pseudohalides. However, in these structures half of the molecules of quin or *i*-quin are outside the central atom coordination sphere.[37,39]

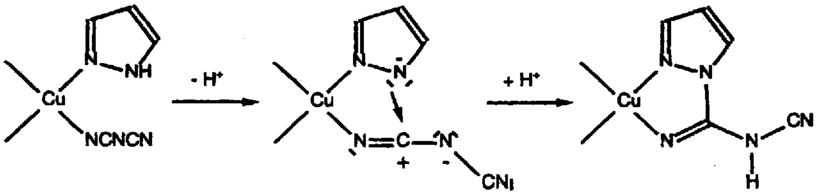
A pair of linkage isomers of composition $[Cu\{N(CN)_2\}_2(iz)_2]$ (α, β) was prepared.[66] These isomers differ in the bridging mode of dicyanamide groups (Scheme 3(b) and (c)). Another type of isomerism was established for $[Co\{C(CN)_3\}_2L_2]$ (L = 2-meiz, 4-meiz).[49] The α-isomer is polymeric and octahedral but the β-form is a monomeric tetrahedral compound. Finally, α- and β-isomers of $[Cu\{C(CN)_3\}_2(pz)_2]$ were prepared.[47] They show pseudo-octahedral geometry and differ by the degree of tetragonal distortion.[96]

9 NUCLEOPHILIC ADDITIONS TO COORDINATED DICYANAMIDE AND TRICYANOMETHANIDE

In 1987 a novel type of nucleophilic addition in the coordination sphere of Cu(II) or Ni(II) was discovered, *viz*, reaction between $[N(CN)_2]^-$ or $[C(CN)_3]^-$ anion and pyrazole or benzopyrazole (indazole).[19] This reaction yields a series of complexes having new anionic chelating ligands of the cyanamido- or dicyanomethanidocarbamoylpyrazolate type. In the case of dicyanamide the imine nitrogen of the pyrazole ring attacks the more positively charged carbon atom of one of the cyanogroups and thus a covalent C(CN)–N(ring) bond is formed; the proton is transferred from the pyrazole nitrogen to the negatively charged amide nitrogen (Scheme 4). With tricyanomethanide, in the new anionic ligand the chain $-N{=}C{-}CH{=}(C{\equiv}N)_2$ is present in place of the chain $-N{=}C{-}NH{-}C{\equiv}N$. On the basis of spectroscopic and magnetic results a probable structure was assigned to $[Cu\{pz\cdot N(CN)_2\}_2]$ as shown in Figure 13.[56]

In following papers[18,21,22,47,55,65] further compounds formed by nucleophilic addition of pyrazole type ligands to dicyanamide or tricyanomethanide in the coordination sphere of Cu(II), Ni(II) and Pd(II) were reported. From some systems products of nucleophilic addition as well as the usual pseudohalide complexes were isolated. Thus, isomeric pairs arose which were called coligand isomers.[18] These isomeric compounds can be unequivocally distinguished by means of their IR spectra.

In the system $Cu(II){-}N(CN)_2^-{-}py{-}CH_3OH{-}H_2O$ another type of nucleophilic addition took place, the product of which was studied by X-ray crystallography (Figure 14).[23,24] The structure of this product, $[Cu(mici)_2]$, showed, that nucleophilic addition of methanol to the cyanocarbon of coordinated dicyanamide led to the formation of a six-membered metallocycle. This reaction is promoted by a coordination activation of the β-carbon of dicyanamide. The Co(III) complex with the same anionic



SCHEME 4 Assumed mechanism of nucleophilic addition in the system $Cu(II){-}N(CN)_2^-{-}pz$.

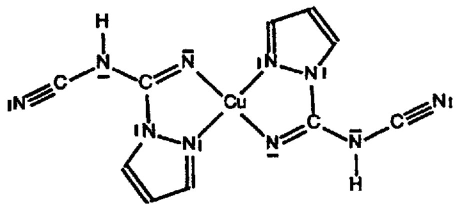


FIGURE 13 Assumed structure of [Cu{pz · N(CN)$_2$}$_2$].

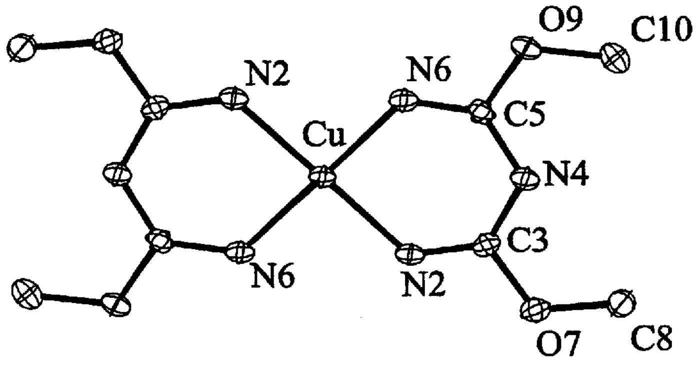


FIGURE 14 Molecular structure of [Cu(mici)$_2$].

chelate ligand has been prepared from the Cu(II) complex in dimethylformamide by treating with cobalt(II) sulfide.[109]

The crystal structure of a dicyanamide compound containing an anionic chelate ligand, (mcoe)$^-$, formed[109] by nucleophilic addition of methanol to nitrosodicyanomethanide in the coordination sphere of Cu(II) was also solved.[91] This compound, [Cu(bpy)(mcoe){N(CN)$_2$}], shows two five-membered metallocycles, one involving the new ligand and the second 2,2′-bipyridine; distorted tetragonal-pyramidal coordination is completed by end-coordinated dicyanamide (Figure 15). The same nucleophilic reaction between coordinated [ONC(CN)$_2$]$^-$ anion and CH$_3$OH was observed also in other systems with Cu(II), Ni(II), Pd(II) and Co(III) as central ions.[110,111]

10 CONCLUDING REMARKS

Information obtained by studying tricyanomethanide and dicyanamide complexes of Cu(II), Ni(II) and Co(II) enable us to draw several conclusions

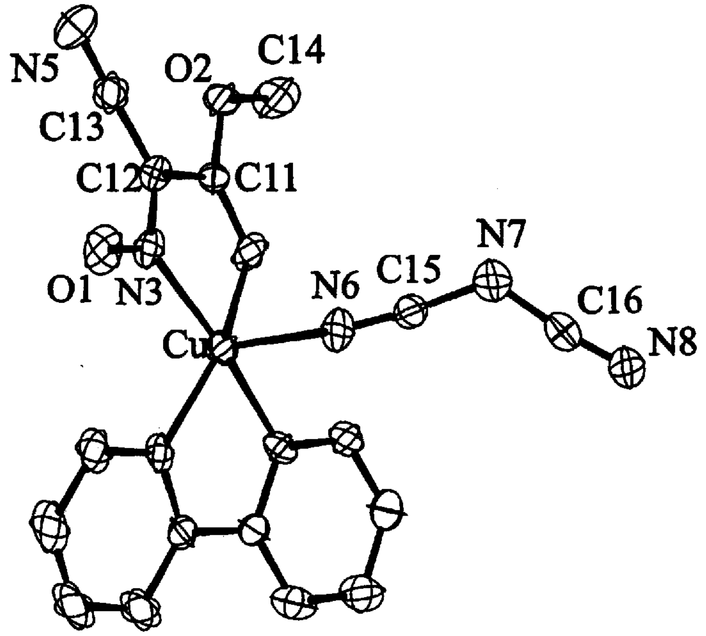


FIGURE 15 Molecular structure of $[Cu(bpy)_2(mcoe)\{N(CN)_2\}]$.

which have a more general validity for characterization of behaviour of $[C(CN)_3]^-$ and $[N(CN)_2]^-$ ions as ligands. These ions show a considerable tendency to function as bidentates and form strong bridges between transition metal atoms. They act as uni- or tridentates rather rarely and usually only under the influence of certain bonding factors in the course of complex formation. The bridging dicyanamide ligand can be bonded by nitrile or rarely by nitrile and amide nitrogen atoms.

Compounds of the type $[MX_2L_n]$ ($n = 2, 4$) having a monomeric structure are uncommon and for their preparation neutral ligands with special properties are needed. Unlike complexes with linear pseudohalides the influence of neutral ligands, mainly α-substituted ones, on the composition and structure of tricyanomethanide and dicyanamide complexes is considerably weaker. Steric effects of these ligands do not govern the structure type but influence some bonding characteristics (ligand field strength, axial interactions, *etc.*).

The compounds $[M\{N(CN)_2\}_2]$, M = Cu(II), Ni(II), Co(II), exhibit exchange interactions and some can be characterized as hard magnets. For bridged tricyanomethanide and dicyanamide complexes of Cu(II), Ni(II) and Co(II) an exchange interaction was also observed. This is ferromagnetic as well as antiferromagnetic in character, resulting in slight overall interaction, reflected in $\chi_M T$ or μ_{eff} *vs.* T functions. In all compounds magnetic interaction is mediated by suitable orbitals (σ and π) of the pseudohalide bridges. Magnetic behaviour at lowest temperatures can be conditioned by long-range magnetic ordering. The tendency of $C(CN)_3$ and $N(CN)_2$ groups to bridge is the most important factor which controls the structure chemistry of coordination compounds of Cu(II), Ni(II) and Co(II) with these ligands.

11 APPENDIX: CRYSTAL STRUCTURES OF SOME OTHER TRICYANOMETHANIDE AND DICYANAMIDE COMPOUNDS

To complete this review we have summarized data concerning crystal structures for tricyanomethanide and dicyanamide compounds of further 3*d* as well as 4*d* and 5*d* elements as central atoms deposited in the Cambridge Crystallographic Database.

11.1 Tricyanomethanide Compounds

In the crystal structure of the rhenium(I) complex, $[Re\{C(CN)_3\}(CO)_5]$,[81] the tricyanomethanide is coordinated as a monodentate *via* the nitrile N-atom at a distance of 2.112(9) Å The crystal structure of $[Fe\{C(CN)_3\}(TTP)]$[83] contains tricyanomethanide anion as a bridging ligand with two of the three nitrile nitrogen atoms bonded to different Fe(III) atoms. The Fe–N distance of 2.317(3) Å suggests weak coordination of the $[C(CN_3)]^-$ anion. The central Fe(III) atom is in a pseudo-octahedral environment. The crystalline compound $[Ru\{C(CN)_3\}(\eta\text{-}C_5H_5)(PPh_3)_2]\cdot CH_2Cl_2$[82] forms discrete $[Ru\{C(CN)_3\}(\eta\text{-}C_5H_5)(PPh_3)_2]$ units with CH_2Cl_2 solvate molecules incorporated in the structure. The central Ru(II) atom is coordinated by two phosphorus atoms from PPh_3 (2.331(3) and 2.327(3) Å), by one nitrogen atom from $[C(CN_3)]^-$ anions (2.071(6) Å) and by the $\eta^5\text{-}C_5H_5$ group (2.222(9), 2.214(10), 2.214(10), 2.217(9), 2.226(8) and 2.217(8) Å). The tricyanomethanide is coordinated as a monodentate *via* the nitrile N-atom at a distance of 2.071(6) Å.

In the crystal structure of $[Rh_2\{C(CN)_3\}(form)_4]$[84] the molecule consists of a dirhodium unit symmetrically bridged by four formamidinate ligands and one $[C(CN_3)]^-$ anion monodentate coordinated in the axial position of a pseudo-octahedrally coordinated central Rh(II) ion *via* the nitrile N-atom at a distance of 2.07(3) Å. The other axial position is completed by second, square-pyramidally coordinated Rh(II) ion. In the refinement there were serious problems with disorder of the tricyanomethanide anion due to its position on the crystallographic four-fold axis.

In $[Ag\{C(CN)_3\}]^{75}$ the tricyanomethanide anion is a tridentate bonded to three different Ag(I) cations with one Ag–N distance of 2.11(6) and two distances of 2.25(4) Å. This arrangement was confirmed elsewhere.[112] The same bonding mode of tricyanomethanide was ascertained in $[Ag\{C(CN)_3\}(phz)_{1/2}]$ with tetrahedrally coordinated Ag(I) (one donor nitrogen from a phz ligand) and in $[Ag\{C(CN)_3\}(pyz)]$ with trigonal-bipyramidal Ag(I) coordination; here two donor nitrogen atoms in *cis*-positions are from two pyz molecules.[112] The Au(I) ion in $[Au\{C(CN)_3\}(PPh_3)_2]^{78}$ is coordinated by two phosphorus atoms with Au–P distances of 2.290(2) and 2.290(2) Å and by a weak interaction with $[C(CN_3)]^-$ anion at a distance of 2.726(11) Å.

In the crystal structure of $[Zn\{C(CN)_3\}_2]^{67}$ the tricyanomethanide ligand is a tridentate bonded to three different central Zn(II) ions in a rutile-like unit cell with four Zn–N distances of 2.120(2) and two distances of 2.211(2) Å. In $[Cd\{C(CN)_3\}(hmt)(H_2O)][C(CN)_3]^{92}$ are two tricyanomethanide anions. One tricyanomethanide is essentially ionic and the second is a tridentate bonded to three different Cd(II) ions to produce an overall rutile-like three-dimensional topology. Both symmetrically independent Cd(II) ions are in special positions with octahedral coordination and the following distances: Cd1–N2 2.292(6), Cd1–N3 2.274(6) and Cd2–N1 2.285(6) Å. In the case of Cd1, octahedral coordination is completed by two nitrogen atoms from two hmt molecules and in the case of Cd2 by two nitrogen atoms from two hmt molecules and two oxygen atoms from two water molecules. The crystal structure of $[Hg_2\{C(CN)_3\}_2]^{77}$ reveals two symmetrically independent molecules. The tricyanomethanide ligand is a tridentate bonded to three different Hg_2^{2+} cations with an Hg–Hg distance of 2.506(1) Å in both molecules. The Hg–N distances are in the range 2.282(8)–2.507(9) Å in a distorted tetrahedral arrangement.

11.2 Dicyanamide Compounds

Although silver and copper are classified as transition metals, the Ag(I) and Cu(I) coordination polyhedra belong to typical non-transition types. The crystal structure of $[Ag\{N(CN)_2\}]^{87,88}$ was studied for both trigonal and orthorhombic modifications. The quality of the crystals was poor but there are no significant differences between the distances and angles in the two forms. Both crystal structures consist of infinite chains. The arrangement around the Ag(I) ion is roughly octahedral in both cases with four longer

Ag–N distances in the trigonal form of 2.91 and 3.08 Å; in the orthorhombic form these are 2.88(2) and 2.98(2) Å. The important difference between the two forms is that in the trigonal form[88] the longer distances are to nitrile N atoms, while in the orthorhombic form[87] two are to nitrile N atoms and two are to amide N atoms.

In the crystal structure of κ-(BEDT-TTF)$_2$[Cu{N(CN)$_2$}Br][89] dicyanamide is bonded as a bidentate *via* two cyanonitrogen atoms. The polymeric anion contains infinite zig-zag chains of $\cdots$Cu–(NC)N(CN)–Cu$\cdots$ units. The central Cu(I) cation is trigonally coordinated by two nitrogen atoms (1.963(7) and 1.941(8) Å) and by the bromide anion.

The crystal structure of [Re{N(CN)$_2$}(CO)$_5$][81] exhibits two independent molecules and monodentate dicyanamide bonded through nitrile N-atoms. The interatomic Re–N bond distances are 2.133(15) and 2.130(16) Å.

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