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CYANATO—COPPER(II) COMPLEXES WITH NITROGEN ORGANIC LIGANDS: PREPARATION, PROPERTIES AND STRUCTURE

J. KOHOUT, M. HVASTIJOVÁ and J. GAŽO

Department of Inorganic Chemistry, Slovak Technical University, 880 37 Bratislava (Czechoslovakia)

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CONTENTS

ABBREVIATIONS

ala	allylamine
an	aniline
bipy	bipyridine
bua	butylamine
bz	benzimidazole
bza	benzylamine
cha	cyclohexylamine

coll	collidine
dabp	diaminobiphenyl
daf	diaminofluorene
dbza	dibenzylamine
dea	diethylamine
dien	diethylenetriamine
dmf	dimethylformamide
dmpz	dimethylpyrazole
dpt	dipropylenetriamine
en	ethylenediamine
et	ethyl
et$_4$dien	1,1,7,7-tetraethyldiethylenetriamine
et$_5$dien	1,1,4,7,7-pentaethyldiethylenetriamine
i-quin	isoquinoline
iz	imidazole
lut	lutidine
me	methyl
me$_2$big	N^1,N^1-dimethylbiguanide
me$_5$dien	1,1,4,7,7-pentamethyldiethylenetriamine
mphbig	morpholinbiguanide
mphda	*m*-phenylenediamine
nia	nicotineamide
ophda	*o*-phenylenediamine
paz	piperazine
pen	propylenediamine
ph	phenyl
phen	phenanthroline
pic	picoline
pip	piperidine
pphda	*p*-phenylenediamine
py	pyridine
pz	pyrazole
quin	quinoline
tld	tolidine
tol	toluidine
tren	2,2′,2″-triaminotriethylamine
urt	urotropine

A. INTRODUCTION

Less attention has been paid to the study of cyanato—copper(II) complexes of transition metals than to other formally related complexes, e.g. with halogen or thiocyanate ligands. Though there may be different reasons for this, it is clear that it is desirable to fill in this gap, in order to know better the behaviour of the NCO$^-$ anion as a ligand and to define the characteristic features and peculiarities of its complexes in the series of pseudohalogeno complexes. The coordination chemistry of the NCO^- anion has already been considered [1—3] within a more extensively treated problem. The present paper is concerned with results concerning cyanato—copper(II) complexes, a study which has been carried out rather systematically in the last ten years. The reasons which led to this study include, besides the importance of copper(II) complexes for many purposes (catalysis, analytical chemistry, biological aspects etc.), also the following facts: copper(II) represents an intermediate between classes "a" and "b"; copper(II) complexes exhibit a great variety of types of coordination polyhedra, often distorted, and they provide advantageous conditions for the occurrence of non-classical types of isomerism.

B. COMPARISON OF THE BONDING PROPERTIES OF THE CYANATE ANION WITH THOSE OF OTHER PSEUDOHALOGENIDE ANIONS

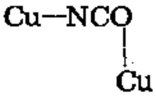
The cyanate anion NCO^- together with CN^-, NCS^-, N_3^- etc. belong to the so-called pseudohalogenide anions [4]. This classification is based on some chemical similarities; these anions differ, however, most particularly in their electronic structure. The electronic structures of pseudohalogenide anions, especially those of NCS^- and NCO^-, were calculated by several authors; the most important results are reviewed in the papers by Rabelais et al. [5], Iqbal [6] and Norbury [3].

In order to appreciate the ligand behaviour of pseudohalogenide anions, we discuss the calculations performed by Hollebone [7] on the basis of the "United Atom" model. According to his results the highest occupied molecular orbital in the NCO^- ion is that which correlates with $4s\sigma$, and is responsible for its Lewis basicity; it is concentrated on the nitrogen end of this ion. No suitable donor orbital appears on its oxygen end. Therefore the NCO^- ion expressly prefers coordination through the nitrogen atom to that through the oxygen atom. On the nitrogen atom there is also the "$2pb_2$" orbital, being relatively stable, but which may be used for bridging bonds with strongly polarizing cations. This may explain why, compared with the N_3^- and NCS^- ions, the NCO^- ion has in general a lower readiness to enter a bridging function. Unlike the N_3^- ion, the cyanate ion does not exhibit π-donor orbitals, but a nearly unique π-acceptor ability into an orbital correlating with $3d_\pi$.

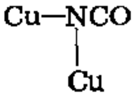
No direct (X-ray structural) method has revealed coordination of the NCO group to the metal atom through the oxygen atom [3]. The low coordination ability of the oxygen atom was explained [8] by its low electron density, compared with that of the nitrogen atom [9]. Curiously MO calculations using the INDO method showed [10] similar electron density on both atoms. Therefore the choice between N— or O—coordination is not influenced [8,11], in contrast to the NCS^- and $NCSe^-$ ions, either by the character of the metal atom ("a" or "b" class), or by the effect (electronic or steric) of the other ligands involved.

The peculiarities of the electronic structure of pseudohalogenide ions [7] also cause different modes of bridge bonding in polynuclear complexes. While for the NCS^- ion at least four modes of bridging are well-known [12—15], the NCO^- ion, in agreement with theoretical prediction, prefers to form one-end N— bridges. These were demonstrated by X-ray structural analysis in the compounds AgNCO [16] and $Cu(NCO)_2(2,4\text{-lut})$ [17]. In addition, IR [18—22] and magnetic [18,22—24] data strongly support the presence of NCO bridges of this kind. Though end-to-end N, O— bridges of the NCO^- ion are improbable [7] for theoretical reasons, they were recently found [25,26] by X-ray analysis in the case of $[Ni_2(tren)_2(NCO)_2](Bph_4)_2$.

From the point of view of bridging of the NCO^- ion, cyanato—copper(II) complexes may be interesting because of the tendency of the Cu^{II} atom to form [27] six- or five-coordinated structures with one or two "semi-coordination" bonds approximately in the axial direction. In such complexes there are possibilities for a "pseudobridging" function of the NCO^- ion. In the formation of weak axial bonds the free oxygen atom (a) or the nitrogen atom (b), which is already coordinated in the equatorial site, may participate.


$\mathrm{Cu{-}NC}\underset{\substack{\vdots\\ \mathrm{Cu}}}{\mathrm{O}}$

(a)


$\mathrm{Cu{-}}\underset{\substack{|\\ \mathrm{Cu}}}{\mathrm{N}}\mathrm{CO}$

(b)

Both modes of axial bonding of the NCO groups may occur depending on the properties of other ligands and on the conditions of the crystal structure packing. Under suitable conditions it was even possible to prepare isomers [22], differing only by the NCO bridging mode. These problems will be dealt with in more detail in the relevant sections.

C. SURVEY OF CYANATO—COPPER(II) COMPLEXES

The first cyanato—copper(II) complexes prepared and described in the literature [27—32] were complexes with pyridine. The preparation of $Cu(NCO)_2$ was reported by Davis and Logan [32] (we failed to reproduce their procedure) and by Söderbäck [33]. The compound $KCu(NCO)_3$ was described firstly by Morgan and Burstall [34], who also obtained crystals of $Cu(en)_2(CH_3OH)_2(NCO)_2 \cdot 4\ H_2O$; we did not succeed in the latter preparation. Ripan isolated the crystalline compounds $Cu(NCO)_2(\alpha\text{-pic})_2$ and $Cu(NCO)_2(dbza)_2$ [35], as well as a complex with urotropine of the composition $Cu(urt)(H_2O)_2(NCO)_2$ [36]. This authoress also reported urotropine compounds in which the water molecules were substituted by two methanol or one ethanol molecule; these compounds, however, do not exist [37]. Ripan [38] further separated compounds with complex cations and anions of the composition $[Co(urt)_2(H_2O)_4][Cu(NCO)_4]$ and $[Cd(urt)_2(H_2O)_4][Cu(NCO)_4]$.

Table 1 lists all cyanato—copper(II) compounds prepared till now, for which values of the effective magnetic moment, μ_{eff}, at room temperature,

TABLE 1

Basic data for cyanato—copper(II) complexes

No.	Compound	Mode of preparation [a]	μ_{eff} (B.M.)	$\tilde{\nu}_{max}$ (μm^{-1})	$\bar{g}$ [b]	Ref.
1	$Cu(NCO)_2$	(a)		≈0.86sh, ≈1.06sh, 1.35		33, 39
2	$KCu(NCO)_3$	(b)	2.02	≈0.70sh, 1.36		19, 33, 40
3	$K[Cu(picolinate)_2(OCN)]$	(c)		1.49		41
4	$Cu(NCO)_2(py)_2$	(c)	1.90	≈1.31sh, 1.64	2.13	11, 42, 43
5	$Cu(NCO)_2(py)_6$	(d)	1.95		2.10	42
6	α-$Cu(NCO)_2(\alpha$-pic$)_2$	(c)	1.87	≈1.48sh, 1.77	2.116	44, 45, 46
7	β-$Cu(NCO)_2(\alpha$-pic$)_2$	(c)		≈1.31sh, 1.66	2.119	47
8	$Cu(NCO)_2(\alpha$-pic$)$	(c)	2.05	1.33		44
9	$Cu(NCO)_2(\beta$-pic$)_2$	(c)	1.84	1.55	2.118	44, 45
10	$Cu(NCO)_2(\gamma$-pic$)_2$	(c)	1.83	1.63	2.107	44, 45
11	$Cu(NCO)_2(2,3$-lut$)_2$	(c)	1.88	≈1.29sh, 1.65	2.119	47
12	$Cu(NCO)_2(2,3$-lut$)$	(c), (e)	2.03	1.30	2.12 [c]	47
13	α-$Cu(NCO)_2(2,4$-lut$)_2$	(c)	1.86	≈1.37sh, 1.71	2.116	22, 44
14	β-$Cu(NCO)_2(2,4$-lut$)_2$	(f)	1.85	≈1.37sh, 1.77	2.115	22
15	γ-$Cu(NCO)_2(2,4$-lut$)_2$	(c)	1.89	≈1.29sh, 1.53	2.129	22
16	$Cu(NCO)_2(2,4$-lut$)$	(c), (e)	2.05	1.33	2.12 [c]	44, 48
17	$Cu(NCO)_2(2,5$-lut$)_2$	(c)	1.86	1.78, 1.95	2.113	47
18	$Cu(NCO)_2(2,5$-lut$)$	(c), (e)	2.00	1.28	2.10 [c]	47
19	$Cu(NCO)_2(2,6$-lut$)_2$	(c)	1.86	≈1.43sh, 1.67, ≈1.93sh	2.105	44, 45
20	$Cu(NCO)_2(3,4$-lut$)_2$	(c)	1.87	≈0.82sh, 1.73	2.105	47
21	$Cu(NCO)_2(3,5$-lut$)_2$	(c)	1.88	≈0.84sh, 1.71	2.102	47
22	$Cu(NCO)_2(2,4,6$-coll$)_2$	(c)	1.83	≈1.45sh, 1.69, 1.97		44, 45
23	$Cu(NCO)_2($quin$)_2$	(c)	1.82	1.56	2.122	11, 45, 49, 50
24	$Cu(NCO)_2($quin$)$	(c), (e)	2.00	1.29		11, 49
25	$Cu(NCO)_2(2$-mequin$)_2$	(c)	1.78	≈1.35, ≈1.63	2.098	45, 49, 50
26	$Cu(NCO)_2(2$-mequin$)$	(c), (e)	2.03	1.41		49
27	$Cu(NCO)_2(4$-mequin$)_2$	(c)	1.81	1.675, ≈1.83	2.100	45, 50, 51
28	$Cu(NCO)_2(4$-mequin$)$	(c), (e)	2.07	1.32		51
29	$Cu(NCO)_2($i-quin$)_2$	(c)	1.85	≈1.36sh, 1.71	2.098	11, 45, 49, 50

TABLE 1 (continued)

Nos.	Compound	Mode of preparation [a]	μ_{eff} (B.M.)	$\tilde{\nu}_{max}$ (μm^{-1})	$\bar{g}$ [b]	Ref.
30	$Cu(NCO)_2(3\text{-me i-quin})_2$	(c)	1.85	≈1.30sh, 1.64	2.130	45, 50, 51
31	$Cu(NCO)_2(3\text{-me i-quin})$	(c), (e)	2.06	1.32		51
32	$Cu(NCO)_2(2\text{-Cl-py})_2$	(c)		1.39	2.150	52
33	$Cu(NCO)_2(2\text{-Cl-py})$	(c)	2.06	1.296	2.11 [c]	52
34	$Cu(NCO)_2(3\text{-Cl-py})_2$	(c)	1.90	≈0.80sh, ≈1.36sh, 1.65	2.127	52
35	$Cu(NCO)_2(4\text{-Cl-py})_2$	(c)	1.81	≈0.81sh, ≈1.38sh, 1.66	2.121	52
36	$Cu(NCO)_2(2\text{-Br-py})$	(c)	2.08	1.31	2.13 [c]	52
37	$Cu(NCO)_2(3\text{-Br-py})_2$	(c)	1.92	≈0.82sh, ≈1.33sh, 1.63	2.131	52
38	$Cu(NCO)_2(4\text{-Br-py})_2$	(c)	1.94	≈0.81sh, ≈1.35sh, 1.675	2.114	52
39	$Cu(NCO)_2(3\text{-I-py})_2$	(c)	1.97	≈0.83sh, 1.64	2.126	52
40	$Cu(NCO)_2(4\text{-NH}_2\text{-py})_2$	(c)	1.89	≈0.86sh, ≈1.41sh, 1.74	2.107	11, 53
41	$Cu(NCO)_2(nia)_2$	(c)	1.85	≈0.81sh, ≈1.33sh, 1.72		54
42	$Cu(NCO)_2(an)_2$	(c)	1.84	1.38, 1.70	2.119	21, 24
43	$Cu(NCO)_2(p\text{-Cl-an})_2$	(c)	1.84	1.31, 1.63	2.128	21, 24
44	$Cu(NCO)_2(p\text{-Br-an})_2$	(c)	1.84	1.32, 1.65	2.114	21, 24
45	$Cu(NCO)_2(p\text{-I-an})_2$	(c)	1.88	1.33, 1.67	2.135	21, 24
46	$Cu(NCO)_2(o\text{-tol})_2$	(c)	1.77	≈1.37	2.112	21, 24
47	$Cu(NCO)_2(m\text{-tol})_2$	(c)	1.85	1.34, 1.71	2.122	21, 24
48	$Cu(NCO)_2(p\text{-tol})_2$	(c)	1.83	1.32, 1.63	2.126	21, 24
49	$Cu(NCO)_2(dea)_2$	(g)	1.81	≈1.53sh, ≈1.84sh, 2.00	2.116	55
50	$Cu(NCO)_2(en)$	(h)	1.87	1.66	2.117	56
51	$Cu(NCO)_2(en)_2$	(h)	1.87	≈1.11sh, 1.42	2.123	56
52	$Cu(NCO)_2(pen)_2$	(c)	1.87	≈1.6–1.8		57
53	$Cu(NCO)_2(paz)_2$	(c)	1.91	≈1.6–1.8		57
54	$\alpha\text{-}Cu(NCO)_2(pz)_2$	(c)	1.74	≈0.81sh, 1.580	2.11 [c]	58
55	$\beta\text{-}Cu(NCO)_2(pz)_2$	(c)	1.80	≈1.34sh, 1.660, ≈1.71sh	2.11 [c]	58
56	$Cu(NCO)_2(iz)_2$	(c)	1.83	1.55	2.110	59
57	$Cu(NCO)_2(N\text{-meiz})_2$	(c)	1.87	1.51, ≈1.795sh	2.118	59
58	$Cu(NCO)_2(2\text{-meiz})_2$	(c)	1.87	1.63	2.139	59
59	$Cu(NCO)_2(2\text{-etiz})_2$	(c)	1.88	1.40, ≈1.73sh	2.122	59
60	$Cu(NCO)_2(1,2\text{-dimeiz})_2$	(c)	1.87	1.56	2.152	59

61	Cu(NCO)$_2$(2-mebz)$_2$	(c)	1.83	1.76		59
62	α-Cu(NCO)$_2$(2-etbz)$_2$	(c)	1.80	≈1.44sh, 1.88	2.106	59
63	β-Cu(NCO)$_2$(2-etbz)$_2$	(c)	1.87	1.61	2.11 [c]	59
64	Cu(NCO)$_2$(mphda)$_2$	(c)			2.15	60
65	Cu(NCO)$_2$(pphda)$_2$	(c)			2.11	60
66	Cu(NCO)$_2$(mphda), 0.5 H_2O	(c)	1.79	1.39, 1.74	2.117	61
67	Cu(NCO)$_2$(pphda), 0.5 H_2O	(c)	1.57	≈1.41	2.117	61
68	Cu(NCO)$_2$(paz)	(c)	1.75	≈1.43sh, 1.77	2.108	61
69	Cu(NCO)$_2$(*o*-tld)$_2$	(c)	2.01	0.925, ≈1.50sh	2.135	61
70	Cu(*o,o*′-dabp)$_2$(NCO)$_2$	(c)	1.87	1.22sh, 1.43	2.134 [c]	42
71	Cu(*m,m*′-dabp)(NCO)$_2$	(c)	1.80	1.11sh, 1.43sh, 1.72	2.090	42
72	Cu(*p,p*′-dabp)(NCO)$_2$	(c)	1.92		2.113	42
73	Cu(2,7-daf)(NCO)$_2$	(c)	1.64		2.104 [c]	42
74	α-Cu(NCO)$_2$(urt)	(i)	1.74	≈1.13sh, 1.355	2.12 [c]	37
75	β-Cu(NCO)$_2$(urt)	(j)	1.82	≈1.28sh, 1.72	2.11 [c]	37
76	α-Cu(NCO)$_2$(urt) · 2 H_2O	(c)		≈1.15sh, 1.46		37
77	β-Cu(NCO)$_2$(urt) · 2 H_2O	(c)	1.78	≈1.16sh, 1.46		37
78	γ-Cu(NCO)$_2$(urt) · 2 H_2O	(k)	1.93	≈1.06sh, 1.32	2.17	37
79	δ-Cu(NCO)$_2$(urt) · 2 H_2O	(c)	1.91	≈1.08sh, 1.34	2.17	36, 37
80	[Cu(Cl-phbig)(NCO)$_2$]	(c)			2.101	62
81	(et$_4$N)$_2$Cu(NCO)$_4$	(l)	1.98	1.15		63, 65
			1.95	1.03, 1.45		64
82	(ph$_4$P)$_2$Cu(NCO)$_4$ blue	(c)	1.92	1.58		64
83	(ph$_4$P)$_2$Cu(NCO)$_4$ yellow	(c)	2.13	1.03, 1.55		64
				1.03, 1.49sh		
84	(ph$_4$As)$_2$Cu(NCO)$_4$ blue	(c)		0.77, 1.57		64
85	(ph$_4$As)$_2$Cu(NCO)$_4$ yellow	(c)	2.19	1.03		64
86	[Cu$_2$(dien)$_2$(NCO)$_2$](Bph$_4$)$_2$	(c), (m)		1.56	2.121 [d]	66, 67
87	[Cu$_2$(dien)$_2$(NCO)$_2$](Bph$_4$)$_2$ · 2 H_2O	(c)	1.888		2.124	66
88	[Cu$_2$(me$_5$dien)$_2$(NCO)$_2$](Bph$_4$)$_2$	(c)	1.84		2.097	68
89	I [Cu$_2$(tren)$_2$(NCO)$_2$](Bph$_4$)$_2$	(c)	2.062	1.00sh, 1.14, 1.49sh	2.100	69
90	II [Cu$_2$(tren)$_2$(NCO)$_2$](Bph$_4$)$_2$	(c)			2.105	69

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[a] See Section D. [b] Calculated from the relation $\bar{g} = \frac{1}{3}(g_\parallel + 2g_\perp)$ or $\bar{g} = \frac{1}{3}(g_1 + g_2 + g_3)$. [c] Determined from the isotropic ESR spectrum. [d] Determined from the spectrum of the Cu-doped zinc(II) complex.

ligand field band maxima, $\tilde{\nu}_{max}$, in the solid state electronic spectra, and average values of the g factor, $\bar{g}$, from the ESR spectra (or at least some of these data) are known.

Besides the compounds listed in Table 1, Burmeister and O'Sullivan [11] prepared compounds of the composition $Cu(NCO)_2L_2$ (L = 4-acetylpy (91), 4-carbomethoxypy (92), 4-CN-py (93), i-nia (94), 4-pyaldoxime (95), 6-nitroquin (96)) and $Cu(NCO)_2L$ (L = 2,2′-bipy (97), 1,10-phen (98)) and they measured their solid state IR spectra, thermal decomposition, electronic spectra and molar conductivities in non-aqueous solutions. Burmeister et al. [67] also isolated $[Cu(et_4dien)(NCO)](Bph_4)$ (99) and $[Cu(et_4dien)(NCO)](Bph_4) \cdot CH_3OH$ (100) and they drew structural conclusions on the basis of molar conductivity data, IR spectra and electronic spectra of solutions in non-aqueous solvents. Gheorghiu and Antonescu [70] prepared $[Cu(me_2big)_2](NCO)_2$ (101) and $[Cu(me_2big)(NCO)_2]$ (102), while Spacu et al. [71] studied the ESR spectra of the latter complex in various non-aqueous solvents and its electronic spectra in dmf. Spacu et al. [72,73] prepared the compounds $[Cu(mphbig)_2](NCO)_2$ (103) and $[Cu(mphbig)(NCO)_2]$ (104). Their spectra in non-aqueous solutions, as well as their ESR spectra in solutions and frozen glasses were studied. Chughtai and Keller [64] presented the preparation of $[ph_4Sb]_2Cu(NCO)_4$ (105). McFadien and Robson [74] prepared $Cu_2(NCO)L$ (L^{3-} = 2-hydroxy-5-methyl-isophthalaldehyde di-2′-mercaptoanil) (106) and measured the temperature dependence of its magnetic susceptibility. Also prepared were compounds of the type $Cu(NCO)_2L_2$ (L = pra (107), bua (108), bza (109), cha (110), pip (111), 3-etpy (112), 4-etpy (113), 3-NH_2py (114)) and $Cu(NCO)_2L$ (L = 2-etpy (115), 2-NH_2py (116), 3-NH_2py (117)) [47,75]. Finally, Hendrickson and co-workers [68] reported the preparation of $[Cu_2(dpt)_2(NCO)_2](Bph_4)_2$ (118) and $[Cu_2(et_5dien)_2(NCO)_2](Bph_4)_2$ (119).

D. OUTLINE OF THE METHODS OF PREPARATION

Preparative methods in copper(II) cyanate chemistry are variant and we can give in this section only a keyword enumeration. The small letters in the parentheses represent the modes of preparation for the compounds listed in Table 1.

(a) By treating $CuBr_2$ with $Hg(NCO)_2$ in acetone.
(b) By the reaction of a saturated solution of $Cu(NO_3)_2$ with KNCO under cooling.
(c) By direct reaction of Cu(II) salt with an alkali metal cyanate and the corresponding nitrogen ligand (or cation) in aqueous, aqueous– methanolic, methanolic, ethanolic or aqueous–ethanolic solutions.
(d) By recrystallization of $Cu(NCO)_2(py)_2$ in hot pyridine.
(e) By splitting-off one mole of the ligand L from the compound $Cu(NCO)_2L_2$, treated with an organic solvent.
(f) By treating the compound $Cu(NCO)_2L$ with vapours of the ligand L.
(g) By the action of volatile ligand L in vapours on $Cu(NCO)_2(2,4\text{-lut})$ the 2,4-

lutidine is removed from the coordination sphere and substituted by the ligand L.

(h) By treating $Cu(NCO)_2(2,4\text{-lut})$ or $Cu(NCO)_2(py)_2$ in methanolic suspension with the ligand L; the ligand replaces the 2,4-lutidine or pyridine in the coordination sphere.

(j) By thermal dehydration of β-$Cu(NCO)_2(urt) \cdot 2\ H_2O$.

(k) By heating γ-$Cu(NCO)_2(urt) \cdot 2\ H_2O$ in some higher alcohol (C_3H_7OH—$C_5H_{11}OH$).

(l) By gentle heating of α-$Cu(NCO)_2(urt) \cdot 2\ H_2O$ in some higher alcohol (C_3H_7OH—$C_5H_{11}OH$).

(m) By replacing the bromide ions in $CuBr_4^{2-}$ by the action of cyanate ions from AgNCO in acetone.

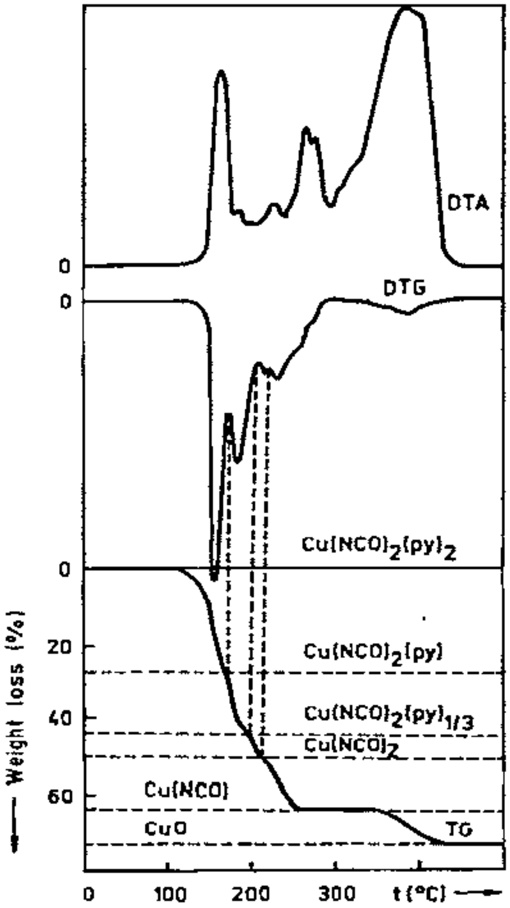


Fig. 1. DTA, DTG and TG curve of $Cu(NCO)_2(py)_2$.

E. THERMAL PROPERTIES

Davies and Ou [30] measured the dissociation pressure of cyanato—copper(II) complexes with pyridine. Porubszky et al. [76] studied the thermal decomposition of compound (4) and found the decomposition course (Fig. 1) to be different from that for cyanato complexes of pyridine with other central atoms. The exothermic processes shown on the DTA curves also indicate redox reactions in addition to the removal of ligands.

Thermal properties of other cyanato complexes of Cu^{II} are limited to the determination of the decomposition temperature [11,21,37,42,44,49,52,61]. The derivatograms of $Cu(NCO)_2L_2$ complexes, where L is a ligand of the pyridine type, are similar to that of the pyridine complex under investigation, the decomposition temperatures of methylpyridine and quinoline complexes being, however, lower than that of halogenopyridine complexes. Especially low decomposition temperatures (below 100°C) have been found for complexes in which the ligands L have the methyl group in the α-position. On the other hand, the isoquinoline complex shows a high decomposition temperature (170°C).

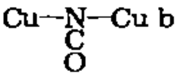
From the thermogravimetric curves of complexes (76)—(79) the stability of the various isomeric forms was determined. The isomers (74) and (75) also differ by their decomposition temperatures [37].

F. X-RAY CRYSTALLOGRAPHIC DATA

X-ray single crystal analysis was completed for complexes (4) [77], (16) [17] and (89) [69,78].

The crystals of complex (4) are tetragonal, space group $I4_1/a$, with $Z = 8$ and $a = b = 15.645(7)$ Å, $c = 9.917(3)$ Å. The final R value is 0.0709. The Cu^{II} atoms are in the centre of symmetry and have square planar coordination formed by two pairs of nitrogen atoms from the two py molecules and the NCO groups. This coordination is completed by two oxygen atoms from two different $Cu(NCO)_2(py)_2$ entities to form a distorted octahedron. The coordination number is 4 + 2 (Fig. 2). The NCO groups appear in the function of pseudobridges Cu—NCO—Cu and thus they link the $Cu(NCO)_2(py)_2$ entities to an infinite three-dimensional framework.

Golub et al. [79] reported interplanar distances for complex (4) and the relative intensities of reflections, obtained on a powdered material.

The crystals of complex (16) are triclinic, space group $\bar{P}1$, with $Z = 2$ and $a = 10.20(3)$ Å, $b = 10.08(8)$ Å, $c = 10.11(2)$ Å, $\alpha = 73.6(2)°$, $\beta = 107.5(2)°$, $\gamma = 145.8(2)°$. The final R value is 0.165. The crystal structure consists of infinite polynuclear chains (Fig. 3), held together by van der Waals bonds. The distances between the Cu^{II} atoms in the chain are by turns 3.22 and 3.44 Å. The nitrogen atoms of the NCO groups have a bridging function between two Cu^{II} atoms, while the oxygen atoms remain uncoordinated. The  $\mathrm{Cu{-}\underset{\substack{C\\O}}{N}{-}Cu}$ bridges are practically coplanar and the bridging angle is 101.55

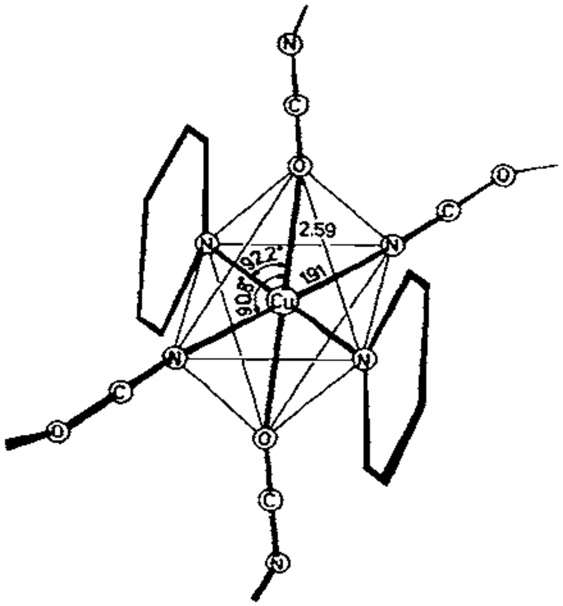
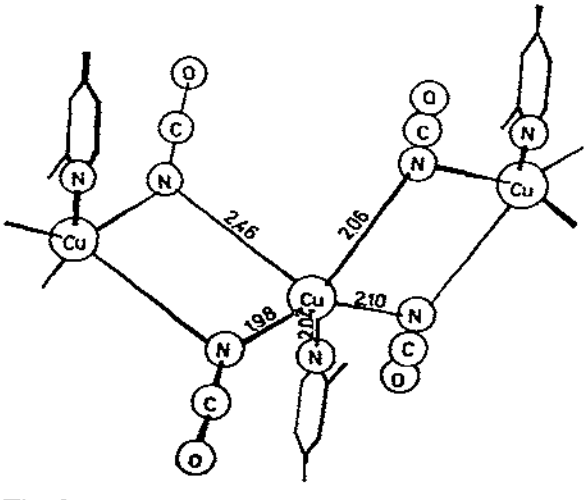


Fig. 2. The Cu^{II} atom environment in $Cu(NCO)_2(py)_2$. Bond lengths in Å. After ref. 77(a).



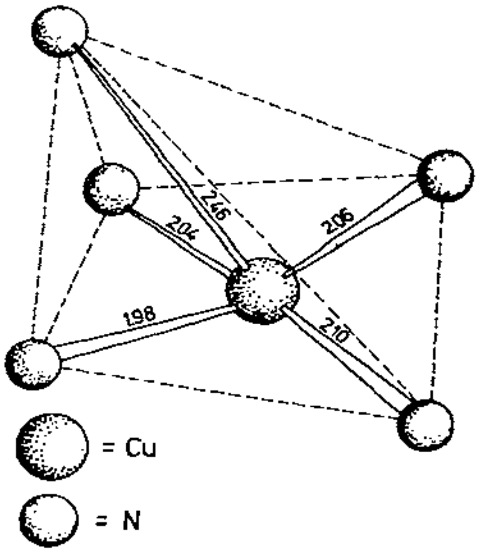


Fig. 3. A part of the infinite chain in $Cu(NCO)_2$(2,4-lut). Bond lengths in Å. After ref. 17.

Fig. 4. The Cu^{II} atom coordination polyhedron in $Cu(NCO)_2$(2,4-lut). Bond lengths in Å. After ref. 17.

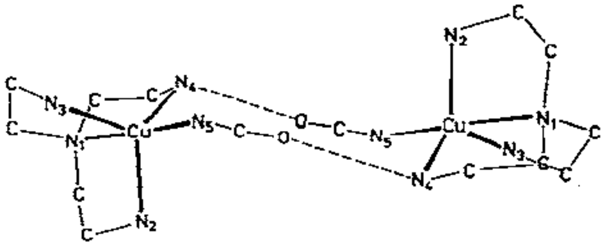


Fig. 5. Structure of the dimeric cation in form I of $[Cu_2(tren)_2(NCO)_2](Bph_4)_2$. The Cu^{II}—N bonds are thicker and the hydrogen bonds are dashed. After ref. 78.

or 99.76°. An approximate sp^2 hybridization may be assumed for the cyanate nitrogen atom. The coordination polyhedron (Fig. 4) is a strongly distorted tetragonal pyramid, which can also be considered as a hybrid of a tetragonal pyramid with a trigonal bipyramid.

Complex (89) crystallizes in the $P2_1/c$ space group with $Z = 2$ and $a = 14.003(6)$ Å, $b = 10.399(5)$ Å, $c = 20.436(9)$ Å, $\beta = 94.00(3)°$. The final R value is 0.075. In the crystal structure discrete $[Cu_2(tren)_2(NCO)_2]^{2+}$ and Bph_4^- units are present. In the dimeric cation (Fig. 5) both Cu^{II} atoms are coordinated in the fashion of a distorted trigonal bipyramid. The trigonal plane angles are ≈112, ≈120 and ≈124°. The distances of the Cu^{II} atoms from the trigonal planes are 0.2310(18) Å. Each NCO group, nitrogen coordinated to one Cu^{II} atom, is simultaneously hydrogen bonded by use of the oxygen atom to the N(4) atom, which is coordinated to the second Cu^{II} atom. The Cu—N distances are: Cu—N(1) = 2.06(1), Cu—N(2) = 2.10(1), Cu—N(3) = 2.08(1), Cu—N(4) = 2.08(1), Cu—N(5) = 1.87(1) Å; the Cu—Cu distance is 6.540(2) Å. The O—N(4) distance of 2.94(2) Å agrees very well with the hydrogen contact.

G. ELECTRONIC METHODS

(i) Magnetic properties

The magnetic susceptibilities of complexes (2), (4), (6), (8)—(10), (13)—(16), (19), (22)—(31), (34), (35), (37)—(39), (42)—(48), (50), (51) and (54) were measured [22—24,40,43,44,48,49,51,52,56,58] at different temperatures from ca. 80—90 K to room temperature; those of complexes (86)—(88) were measured [66,68] down to 4.2 K. Most of these complexes are magnetically dilute. Their corrected molar susceptibilities χ_M^{corr} follow the Curie law or rather the Curie—Weiss law $\chi_M^{corr} = C(T + \theta)^{-1}$ or $\chi_M^{corr} - N_A\alpha = C(T + \theta)^{-1}$ for small values of the Weiss constant θ(≈5 K > $|\theta|$ > 1 K). Thus, the effective magnetic moments μ_{eff} are only slightly temperature dependent. Table 2 presents magnetic data for complexes with θ values and temperature dependence of μ_{eff} indicating a perceivable interaction between the Cu^{II} atoms. This

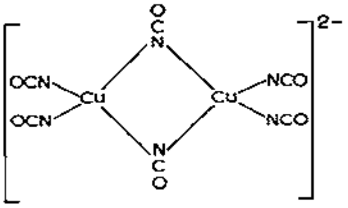
TABLE 2

Magnetic data for cyanato—copper(II) complexes with exchange interaction

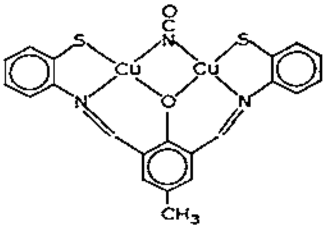
Complex	μ_{eff}(B.M.)/T(K)	C(c.g.s.u. Kmol^{-1})	θ(K)	$2J$ (cm^{-1})	Ref.
(2)	2.02/294 2.12/94.4	0.507	—9.22	+220^{a}	40
(15)	1.92/293 1.98/93	0.448	—10	+9^{b}	22
(16)^{c}	2.02/294.5 2.11/88	0.468	—24	+17^{b}	48
(43)	1.84/293 1.70/82	0.457	+23		24
(44)	1.84/293 1.78/82	0.433	+8		24
(46)	1.77/293 1.55/77	0.445	+41	—20^{b}	24
(47)	1.85/293 1.72/82	0.454	+18		24
(48)	1.83/293 1.71/82	0.440	+16		24
(106)		d	d	—200^{a}	74

^{a} Bleaney—Bowers model. ^{b} Ising model. ^{c} Other structurally and magnetically similar complexes are not included in the table. ^{d} The Curie—Weiss law is not obeyed.

interaction reveals the presence of bridging NCO groups, which make possible a transmission of the copper(II) unpaired spins.



(I)



(II)

The magnetic susceptibilities of complexes (2) and (106) are in agreement with the Bleaney—Bowers model [80], so that binuclear bridged arrangements (I) and (II) can be postulated for these compounds.

The temperature dependence of the susceptibilities for complexes (15), (16) and (46) conforms with the anisotropic Ising model [81] (in the case of complex (16) only down to ca. 150 K). In the chain (OCN)N—bridged complex (16) the ferromagnetic coupling apparently is achieved [48] by means of the σ-orbitals of both Cu^{II} atoms interacting with different bridge sp^2-orbitals being mutually orthogonal. Complexes (8), (12), (16), (18), (24), (26), (28), (31), (33) and (36) display a similar magnetic behaviour [47,49—52]. A polynuclear chain structure (Fig. 6) was also assumed [23,24] for the antiferromag-

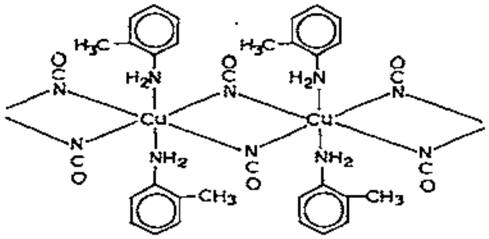


Fig. 6. Assumed structure of $Cu(NCO)_2(o\text{-tol})_2$.

netically coupled complex (46). The occurrence of magnetic interaction of both signs for bridged cyanato—copper(II) complexes is very probably conditioned by the influence of NCO bridge symmetry. The ferromagnetic interaction found [22] in complex (15) suggests a structure with Cu—NCO axial links, the participating NCO groups being from the adjacent structural units. Slight exchange demagnetization in complexes (43), (44), (47) and (48) is explained [23,24] by suitable crystal structure packing.

The high magnetic moments of complexes (69), (78), (79), (81), (83) and (85) in accordance with other data may infer a distorted tetrahedral environment of the Cu^{II} atom [37,61,63,64].

(ii) ESR spectra

ESR spectra were measured mostly on polycrystalline samples in X-band [22,24,37,40,42,45,47,48,52,53,55,56,58—62,66,68,69,71,72,82]. Essentially they are of the following types: (a) normal axial, (b) normal orthorhombic, (c) reversed axial, (d) reversed orthorhombic, (e) isotropic or pseudoisotropic, (f) triplet state ($S = 1$) spectrum. Typical examples are shown in Fig. 7.

The most frequent ESR spectra are the normal axial ones; they are produced by complexes (5)—(7), (9)—(11), (13)—(15), (17), (19)—(21), (23), (25), (27), (29), (30), (32), (34), (35), (37)—(40), (46), (49), (56)—(60), (62), (64), (65), (67), (68), (72), (78)—(80), (86) and (87). The g factors obtained from these spectra, except for complexes (78) and (79), are in agreement [83] with the elongated tetragonal geometry having a $d_{x^2-y^2}$ ground state. The values of $G = (g_\parallel - 2)/(g_\perp - 2)$ [83,84] are greater than 3.5, except for complexes (64), (65), (86) and (87), so that the crystal g values are very close to the true g factors of the Cu^{II} atom local environment.

The ESR spectra of complexes (78) and (79) [37] are characterized by a parallel copper hyperfine splitting (Fig. 8). The values of $A_\parallel$, $g_\parallel$ and $g_\perp$ gauged as 80 Oe, 2.3 and 2.1, respectively, are indicative for the Cu^{II} atom in a field of pseudotetrahedral symmetry.

Hendrickson and co-workers measured [66] the Q-band spectrum of the complex (87) at room temperature (Fig. 9). Its parallel component shows nine copper hyperfine lines, indicating a weak exchange interaction in the dimeric cation with a small zero field splitting.

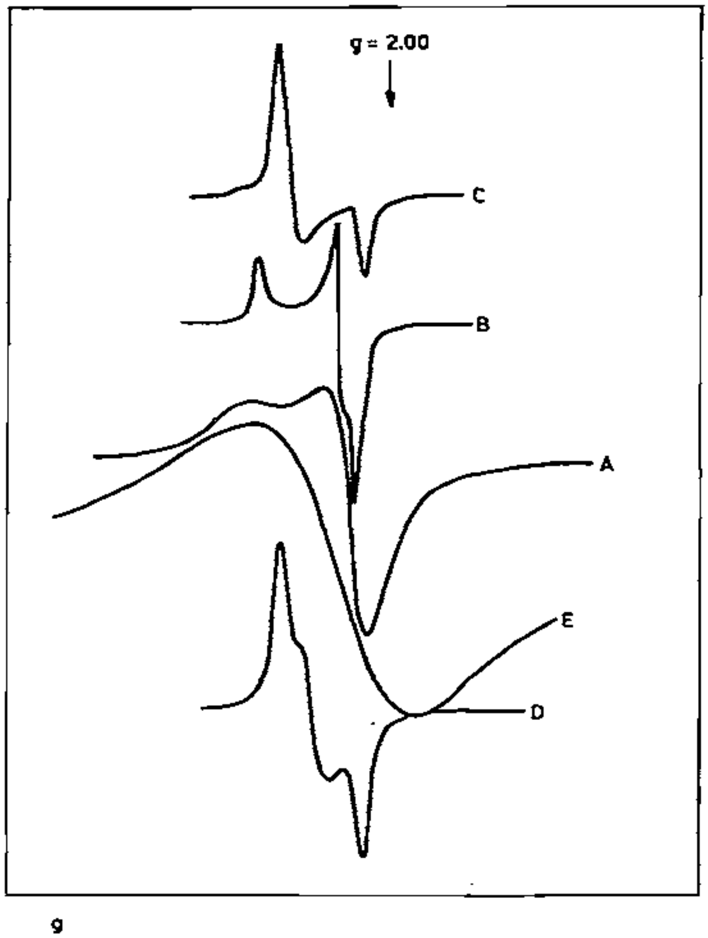


Fig. 7. Typical examples of ESR spectra for cyanato—copper(II) complexes.

A normal orthorhombic spectrum occurs only for complexes (42), (71) and (88); in the first the $g_\perp$ anisotropy is small [24]. For complex (71) [42] the value of $R = (g_2 - g_1)/(g_3 - g_2)$ [85,86] equalling 1 may reveal a ground state given by a mixture of the d_{z^2} and $d_{x^2-y^2}$ functions or more likely, an exchange coupling through misaligned molecular axes. The Q-band spectrum of complex (88) [68] exhibits ten copper hyperfine lines on the parallel signal, suggesting the presence of an exchange interaction where $|J| < \approx 0.5$ cm^{-1} In the X-band spectrum there are seven copper hyperfine lines visible on the $\Delta M_S = 2$ absorption. It was deduced, that in this compound two NCO groups are most probably involved in the end-to-end bridging function.

A reversed axial spectrum was found for complexes (45), (89) and (90) and a reversed orthorhombic spectrum for complexes (4), (43), (44), (47), (48) and (51). Complexes (89) and (90) [69] display in Q-band spectra, $g_\parallel$ values

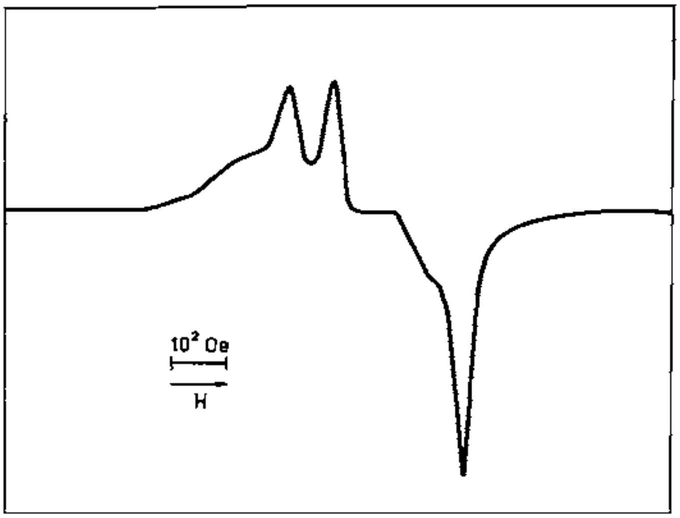


Fig. 8. ESR spectrum of γ-$Cu(NCO)_2(urt) \cdot 2H_2O$.

very near to 2.00, thus indicating a trigonal bipyramidal Cu^{II} atom environment with a d_{z^2} ground state. The X-band spectrum of any form (Fig. 10) contains, in addition to the $\Delta M_S = 1$ signal, a line corresponding to the $\Delta M_S = 2$ transition and two lines assignable as triplet ← singlet transitions. From the temperature dependence of the positions of the last two lines it was determined that the exchange parameter J varies between ≈340 and 95 K for form (89) from 0.09 to 0.16 cm^{-1}, while for form (90) only from 0.05 to 0.06 cm^{-1}.

The reversed spectra of complexes (4) [42], (43)—(45), (47) and (48) [24] cannot be due to the d_{z^2} ground state, but they are probably conditioned by exchange interaction between crystallographically inequivalent $Cu(NCO)_2L_2$ molecules with their principal axes inclined by about 90°. The

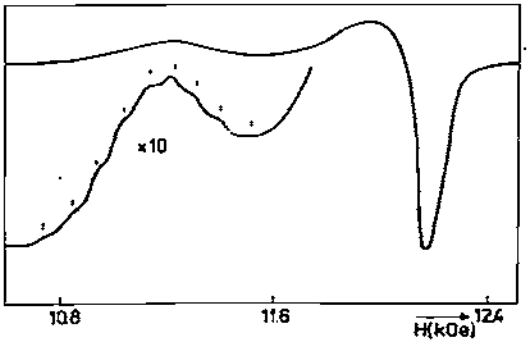


Fig. 9. Q-band ESR spectrum of $[Cu_2(dien)_2(NCO)_2](Bph_4)_2 \cdot 2H_2O$.

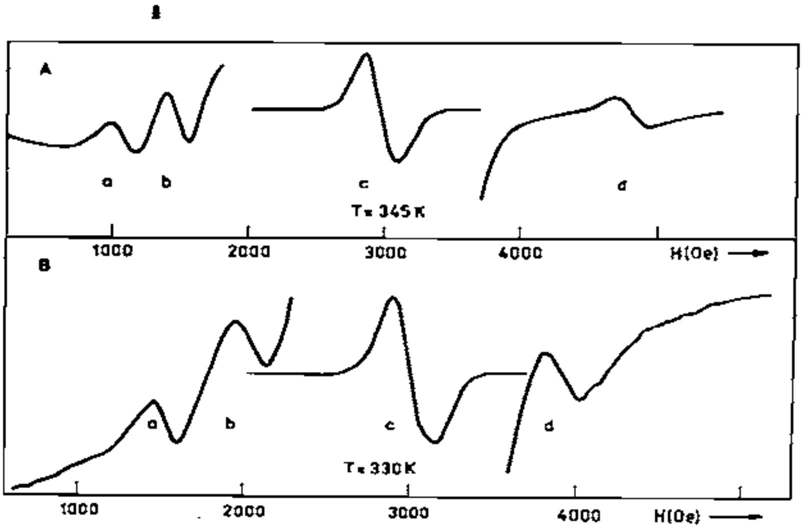


Fig. 10. X-band ESR spectrum of $[Cu_2(tren)_2(NCO)_2](Bph_4)_2$, form I(A) and form II(B). (a) triplet ← singlet transition; (b) $\Delta M_S = 2$ transition; (c) $\Delta M_S = 1$ transition; (*d*) triplet ← singlet transition.

spectrum of complex (51) [56] with $R = 1.05$ can likewise be accounted for by misalignment of the molecular axes.

Isotropic or pseudoisotropic (with a visibly asymmetric single line) spectra are produced by complexes (12), (16), (22), (54), (55), (61), (70), (73)—(75), (101) and (104); the spectra of complexes (18), (33), (36), (63), (76) and (77) approach the isotropic type. The most frequent reason for this type of spectra for cyanato—copper(II) complexes seems to be extensive exchange coupling operating between the Cu^{II} atoms through the bridging NCO groups, as was established [48] for complex (16).

Complex (2) exhibits [40] in its ESR spectrum both low and high field lines, which may be assigned to the transitions between the M_S levels of the triplet state, stabilized owing to a spin interaction between the Cu^{II} atoms in a binuclear system.

(iii) Electronic spectra

The electronic spectra of solid cyanato—copper(II) complexes provide the basic data for consideration of the symmetry of the Cu^{II} atom local environment [83,86]. Based on the shape, number and position of the ligand field bands ($d \leftarrow d$ bands), these spectra may be divided into six main groups (Table 3). Though this division is not sharply limited, since some types overlap and some intermediate types occur, it provides a useful survey of the kinds of coordination geometry available for cyanato—copper(II) complexes. As we can see from Table 3, the electronic $d \leftarrow d$ spectra of cyanato—copper(II)

TABLE 3

Solid state electronic spectra of cyanato—copper(II) complexes

Type of spectrum	Approximate range of $d \leftarrow d$ peaks (μm^{-1})	Coordination geometry	Compounds
A	1.4—1.6[a]	Pseudooctahedral	(9), (15), (23), (58), (60), (70), (82)
B	1.6—1.9 1.3—1.5sh[b]	Strongly tetragonal	(6), (7), (13), (14), (25), (27)[c], (29), (30), (42)—(45), (47), (48), (50), (52), (53), (57)[c], (61), (62), (66), (68), (75)
C	1.9—2.0 1.7—1.85 1.4—1.5sh[b]	Nearly planar	(17), (19), (22), (49)
D	1.6—1.75[d] 0.8—1.1sh	Pseudooctahedral, weakly distorted	(20), (21), (34), (35), (37)—(41), (54)
E	1.3—1.65[e]	Five-coordinate	(3), (8), (11), (12), (16), (18), (24), (26), (28), (31)—(33), (36), (59), (74), (76), (77), (86), (89), (90)
F	1.0—1.45 0.7—1.1[b]	Distorted tetrahedral	(1), (2), (78), (79), (81), (85)
A→B	1.55—1.65[e]	Intermediate A—B	(10), (55), (56), (63)
A→F	1.5—1.6 0.8—1.0	Intermediate A—F	(69), (83), (84)

[a] An unresolved shoulder on the side of low wavenumbers sometimes occurs. [b] In a few cases this peak does not occur. [c] A high-wavenumber shoulder instead of that at lower wavenumber occurs. [d] An unresolved shoulder between ca. 1.3—1.4 μm^{-1} sometimes occurs. [e] A shoulder on the low wavenumber side frequently occurs.

complexes display the presence of tetragonal Cu^{II} species submitted to axial distortion of different degree, from pseudooctahedral to practically planar geometry, and also five-coordinate and pseudotetrahedral polyhedra of Cu^{II}

(iv) Structural conclusions

The Cu(NCO)$_2$L$_2$ complexes, where L is a monodentate ligand such as pyridine, primary amine, pyrazole or imidazole, show basically elongated tetragonal *trans* structures (possibly with a weak orthorhombic distortion). These structures are formed by planar units involving short equatorial Cu—NCO and Cu—N(L) bonds. Thereby they are mutually placed in such a way that long axial bonds of the Cu^{II} atom with the donor atoms of the NCO groups of the adjacent units arise (Fig. 11). Thus the crystal structures of the complexes contain polymeric aggregates, in which every Cu^{II} atom has the coordination number 4 + 2, 4 + 1 + 1 or 4 + 1 (see Fig. 1 of ref. 87).

The structure of some Cu(NCO)$_2$L$_2$ complexes should be particularly men-

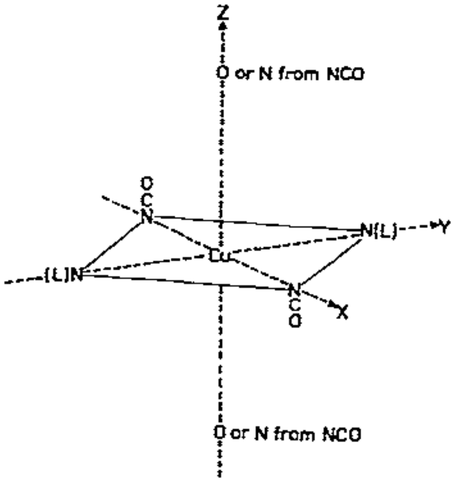
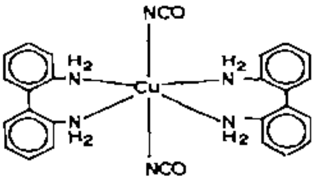


Fig. 11. Scheme of the Cu^{II} atom environment in the $Cu(NCO)_2L_2$ complexes (L = monodentate ligand).

tioned. Complex (69) exhibits [61] a pseudotetrahedral molecular structure with monodentate *o*-tld ligands. Complex (70) probably contains [42] in the equatorial plane two seven-membered chelate rings, completed by two *trans*-coordinated NCO groups. Nevertheless, the bidentate mphda and pphda ligands in complexes (64) and (65) can bridge the Cu^{II} atoms with *trans*-coordinated NCO groups in infinite two-dimensional networks.



(64)

The $Cu(NCO)_2L$ complexes, where L is a monodentate, sterically hindering ligand of the pyridine type, according to very consistent electronic properties all exhibit a structure closely related to that of complex (16) determined [17] by X-ray crystallography (see section F).

The remaining complexes of composition $Cu(NCO)_2L$ or $Cu(NCO)_2L \cdot n\ H_2O$ utilise polydentate ligands. Complex (50) very probably displays [56] in-plane *cis*-CuN_2(2 NCO)N_2(en) species with an axial interaction from the NCO groups of the adjacent molecules. The basis of the structure for complexes with bridging ligands L are infinite chains ...—Cu—N(L)N—Cu—N-(L)N—..., in which every Cu^{II} atom is in addition coordinated with two NCO groups. The arrangement of the basic CuN_4 chromophores in chains may be coplanar or pseudotetrahedral. The former case occurs e.g. for complexes (66)—(68), (71), (72) and (74)—(77), the latter for complexes (78) and (79).

For coplanar CuN_4 chromophores the Cu^{II} atom attains a higher coordination number (five or six) by axial bonds with the NCO groups of the adjacent chains.

Complexes (86) and (87) probably contain [66] dimeric cations, in which coplanar $CuN(NCO)N_3(dien)^+$ species are associated by hydrogen bonding between the NCO group coordinated to one Cu^{II} atom and a primary nitrogen atom of the dien ligand coordinated to the other Cu^{II} atom.

(v) Solution spectral studies

Spectrophotometric measurements were used to study the formation, composition and the relative stability of cyanato—copper(II) complexes in water [88], acetone [89,90] and methanol solutions [91,92].

Chughtai and Keller [64] measured the absorption spectra of complexes (81)—(85) in chloroform, dichloromethane, nitromethane and acetone from —55°C up to 45°C. According to their results, the originally pseudotetrahedral configuration of the $[Cu(NCO)_4]^{2-}$ anion successively changed towards a square planar geometry, the relative degree of the change depending also on the character of the solvent.

Pflaum and Brandt [93] recorded the absorption spectra of cyanato—copper(II) complexes with pyridine and its homologues, extracted into chloroform. The absorption spectra of complexes (4), (6), (8)—(10), (13), (16), (19), (22)—(31), (40), (42)—(48), (66), (67), (69)—(71) were measured [11,21,42,61,94] in various non-aqueous solvents of different basicity. Most spectra revealed ligand field bands indicative of distorted octahedral Cu^{II} species, in which some coordination sites are occupied by solvent molecules. Sterically hindered complexes (6), (13), (19), (22), (23), (25), (27) and (30) probably split off one ligand molecule by the action of solvent [94]. Complex (46) in acetone, methanol and chloroform, as well as complexes (47) and (48) in chloroform are not subject to coordination of solvent [21]. The absorption spectra of complexes (66) and (67) in dmf suggest [61] the presence of tetrahedrally distorted planar species, formed apparently in the dissolving process. The spectrum of complex (69) in dmf exhibiting four $d \leftarrow d$ peaks below 1.5 μm^{-1} indicates [61] that the solution contains pseudotetrahedral species, as does the solid compound.

The solution spectra of complexes (70) and (71) in dmf were interpreted [42] by an exchange of the coordinated NCO groups for solvent molecules. However, such considerable changes do not seem to be very likely, especially in the absence of any other supporting data.

H. INFRARED SPECTRA

(i) Vibrations of the cyanate group

The infrared vibrations of the NCO^- ion and their variation caused by coordination have been dealt with in general [2,3,95—97]. Table 4 shows fundamental vibrations of the NCO group in some selected copper(II) complexes. The ν_{as}(NCO) vibration appears as a very strong and broad band (often with a certain side-splitting) in the range ca. 2270—2150 cm^{-1}. The ν_s(NCO) vibration occurs generally as a weak to medium band in the range ca. 1370—1300 cm^{-1}. The values of ν_s confirm that the NCO group is N-bonded in all cyanato—copper(II) complexes. On the basis of thermodynamic considerations an O-bonded NCO group was postulated for complex (3); this exhibits a band at

TABLE 4

Cyanate vibrations (cm^{-1}) [a] for selected cyanato—copper(II) complexes

Complex	ν_{as}(NCO)	ν_s(NCO)	δ(NCO)	Ref.
KCNO	2165	1301.5	637	95
		1207	628	
(2)	2268vs	1342ms	698ms	40
	2252vs	1312m [b]	656s	
	2215vs	1288mw [b]	637s	
	2152s		612sh	
			606s	
(4)	2208	1320	625	11
			611	
(9)	2247vs	1334m	673vw	20
	2227vs		640w	
	2197vs		631vw	
			616mw	
			607sh	
(10)	2225vs	1345s	618m	20
(13)	2218vs	1343s	615vs	22
		1326m	604vs	
(15)	2218vs	1347sh	650mw	22
	2190vs	1340w	618s	
			611sh	
(33)	2203vs	1317vw	668mw	52
	2163vs		616s	
(46)	2258s	1367m	683vw	21
	2207s		634w	
			613sh	
			604m	
(47)	2230vs	1344ms	632ms	21
			609ms	
(81)	2247sh	1328w	619m	98
	2183 vs		617m	
			612sh	
	2200s	1324m	618m	64,65
(97)	2236	1322	617	11
	2189	1310	606	

[a] Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder.
[b] The assignment 2δ(NCO) is also possible.

$\approx$1200 cm^{-1}, which is, however, more likely the 2δ overtone than the ν_s(NCO) stretch [41].

The δ(NCO) vibration, doubly degenerate in the free ion, gives rise to bands of variable intensity (weak to strong) in the range ca. 700—600 cm^{-1}. If a single δ(NCO) band occurs, which may be weakly split (as for KNCO), terminally bonded NCO groups may be supposed (but see later). If, however, two or more bands separated by $\approx$30—90 cm^{-1} correspond to the δ(NCO) vibration, the NCO groups are very probably involved in bridging of the type >NCO. According to the δ(NCO) mode, N-bridged (or pseudobridged) NCO groups are contained in the compounds (2), (8), (9), (11), (12), (15), (16), (18), (23), (24), (26), (28), (31), (33), (36), (46), (58), (63) and (74)—(77).

Of topical interest is the question of the influence of a pseudobridging end-to-end function of the NCO group with axial Cu—OCN linkage on the behaviour of the δ(NCO) mode. For complex (4), which has such an NCO group function (see section F), the δ(NCO) vibration is split [11,42] little more than for KNCO. Complexes (34), (35) and (37)—(39), which probably likewise contain a Cu—OCN linkage, exhibit [52] the δ(NCO) mode similarly weakly split or even unsplit. Thus it seems that the pseudobridged N,O-bonding of the NCO group is not distinctly manifested by behaviour of the δ(NCO) mode. The δ(NCO) vibration is split [21,54a] in the range $\approx$25—35 cm^{-1} in complexes (41), (43), (47) and (48), so that the mode of NCO pseudobridging is not clear.

The ν_{as}(NCO) vibration is split into two or more components of similar intensity in several cases. This splitting may be caused by a low symmetry of the coordination polyhedron, as it is for the distorted five-coordinated [20, 47,52], pseudotetrahedral [40,98] or *cis*-square planar configurations [11,56]. In some cases, however, the splitting of both ν_{as}(NCO) and ν_s(NCO) may be conditioned by the crystal site symmetry or by correlation field effects.

An unusually manifold splitting of the NCO vibrations found [19,40] for complex (2) indicates the presence of both terminally bonded and bridged NCO groups; this is, however, inevitable in a binuclear structure (see Section G,(i)).

(ii) Far infrared vibrations

The Cu—ligand stretching vibration data for cyanato—copper(II) complexes are summarized in Table 5. Frequencies that may be assigned to the Cu—NCO stretch occur in the range of about 410—340 cm^{-1}. Of course, owing to coupling with other modes, they are not considered to be pure modes; the same is true for the Cu—N(L) stretches.

Systematic study was devoted [52,59,99] to the far IR spectra of cyanato—copper(II) complexes with ligands of the pyridine and imidazole groups ((4), (6), (9)—(11), (13)—(15), (17), (19)—(21), (34), (35), (37)—(39) and (56)—(63)). From the frequency shifts of the Cu—NCO and Cu—N(L) stretches in mono- and dimethylpyridine complexes compared with those in the pyridine

TABLE 5

Cu—ligands stretching frequencies (cm^{-1})[a] for cyanato—copper(II) complexes

Complex	ν(Cu—NCO)	ν(Cu—N(L))	Ref.
(2)	352		40
(4)	378s	258s	99
(6)	388s	278sh 249s	99
(9)	378s	263s	99
(10)	374s	266s	99
(11)	373ms	233ms	99
(12)	386sh 369ms	270ms[b] 252sh[b] 226mw	47
(13)	393s	246s	22,99
(14)	393s	270w 274s	22
(15)	380s	255s	22
(16)	400sh 371s	265m 253sh	47
(17)	395s 364sh	256s	99
(18)	366ms	273m 226mw	47
(19)	394s	242s	99
(20)	374s	267s	99
(21)	383s	262s	99
(33)	396sh 374s	272mw 239mw	52
(34)	380s	267s	52
(35)	377s	269s	52
(36)	378sh 370s	269mw 234mw	52
(37)	381s	267s	52
(38)	382s 374s	260s	52
(39)	382s 376sh	267s	52
(41)	310sh 262sh		54a
(49)	388s	453m 429w	55
(50)	405m 390sh	[c]	56
(51)	380mw	[c]	56
(54)	367s	291s 260m	58
(55)	365s	288s 256ms	58
(56)	357s	291s 269ms	59
(57)	364s	296ms 282sh	59

TABLE 5 (continued)

Complex	ν(Cu—NCO)	ν(Cu—N(L))	Ref.
(58)	357s	297ms	59
(59)	369s	253m	59
(60)	354vs	273s	59
(61)	379vs	253s	59
(62)	380vs	276s [b]	59
(63)	383vs	258ms	59
(66)	404sh 378vs	486w	61
(67)	356s	492s	61
(68)	356s	417m	61
(69)	376s	[d]	61
(74)	404s 385s 377sh	258ms	37
(75)	407s 392s	266s	37
(77)	400s 387s	264s	37
(78)	382ms [b] 366s	256m	37
(79)	384ms [b] 367s	260m	37
(81)	338s		65, 98
(82)	375 355		64
(83)	370 355		64
(84)	360 [b]		64
(85)	365 [b] 350 [b]		64

[a] For abbreviations see footnote [a] to Table 4. [b] Cannot be distinguished from the ligand or cation absorption. [c] The ν(Cu—N(L)) mode cannot be distinguished from that of ν(Cu—NCO). [d] Cannot be determined for the ligand absorption.

complex, a mutual relationship of the Cu—NCO and Cu—N(L) bonds was established. This is particularly perceptible if the ligands exert steric effects (α-methylsubstituted pyridines); similar behaviour was observed [99,100] for analogous thiocyanato—copper(II) complexes. The low basicity of the halogenopyridines, however, exhibits no marked influence on the strength of the Cu—N(L) bond. In the group of imidazole complexes the skeletal stretches again are influenced by the ligand steric hindrance, though the circumstances are in some cases less obvious here.

For complex (81) with a distorted tetrahedral geometry a single band below 340 cm^{-1} was assigned [65,98] to the Cu—NCO stretch, though two bands might be expected [98]. Chughtai and Keller suggest [64] that the green substance considered to be complex (81) is a mixture of two forms and the ≈340 cm^{-1} band can be composed of two bands (with shoulders). One strong band [98] or two weak bands [65] in the range 250—200 cm^{-1} were attributed to the Cu—NCO deformation mode. Complex (2) containing the pseudotetrahedral $[Cu_2(NCO)_6]^{2-}$ anions exhibits [40] a single (though broad and diffuse) Cu—NCO stretching band and two Cu—NCO deformation bands around 250 cm^{-1}.

I. STRUCTURAL FACTORS IN CYANATO—COPPER(II) COMPLEXES

(i) General remarks

For Cu^{II} compounds experimental data show the existence of a great number of coordination geometries [83,101,102], but especially shapes formed by distortion of a certain basic geometry [83,87,103—105]. This fact was theoretically substantiated by Gažo et al. [87] based on the theory of vibronic interactions in electronically degenerate states [106], leading to the occurrence of distortions of the Jahn-Teller or pseudo-Jahn-Teller type as an intrinsic feature of the d^9 configuration of the Cu^{II} atom. However, adaptation of some from many possible distorted configurations is governed by external influences. Thus we directed our study to the problem of what factors influence the structure-bonding characteristics of cyanato—copper(II) complexes.

In the series of $Cu(NCO)_2L_2$ complexes (L = methylsubstituted pyridine) [20,44,45,47,99] significant influence is exerted by the steric effect of α-substituted ligands. Complexes with these ligands generally are axially more distorted than those with ligands without a perceptible steric hindrance. Moreover, more stable $Cu(NCO)_2L$ complexes with lower coordination number are formed with sterically hindering ligands. Complexes (19) and (22) are exceptions, their relative stability seems to be connected with their nearly coplanar geometry. Even when ligands do not show any steric effect, their influence on the structure of $Cu(NCO)_2L_2$ complexes is observable, apparently due to crystallostructural effects and electronic cooperation with the NCO groups.

In the case of $Cu(NCO)_2L_2$ complexes, where L = quinoline or isoquinoline [11,20,45,49—51], steric hindrance of the ligands makes possible again the change to five-coordinate $Cu(NCO)_2L$ complexes. In other respects, however, the ligand steric effect is shown less conspicuously.

With 2-halogenopyridines as ligands, unlike 2-methylpyridines, the formation of five-coordinated $Cu(NCO)_2L$ complexes is very much preferred [52]. Apparently the mutual effect of ligands, steric and electronic, is responsible for this peculiarity. Furthermore, $Cu(NCO)_2L_2$ complexes, where L = 3- or 4-halogenopyridine [52], exhibit very similar coordination geometry and complexes with 3-halogenopyridines are isostructural. Accordingly, the structural effect of the 3- or 4-halogen substituent is less pronounced in comparison with the methyl substituent.

For $Cu(NCO)_2L_2$ complexes with L = an aniline type ligand [21,23,24] *m*- or *p*- substitution in aniline by methyl or halogen does not influence the coordination geometry, but brings about changes in the mutual position of molecules in the crystal structure.

In the series of $Cu(NCO)_2L_2$ complexes, where L = an imidazole type ligand [59], increase of tetragonal distortion is conditioned mainly by the effect of the benzene ring in alkylbenzimidazole ligands; substitution on the imidazole ring appears to be less effective.

(ii) Isomerism with cyanato—copper(II) complexes

The occurrence of stereo-bonding isomers of copper(II) complexes, including distortion isomers [87,107], may be considered a manifestation of the plasticity of the Cu^{II} coordination sphere. For several cyanato—copper(II) complexes different modifications were isolated and studied, and may be considered as stereo-bonding isomers. We will present here a brief survey of such cases.

The preparation of isomeric cyanato—copper(II) complexes is conditioned in general by a number of factors influencing the chemical equilibrium. More specifically for the preparation of various isomeric compounds different temperatures can be employed in the preparation process [37,58,59], small changes made in the molar ratios of the reactants [22,44,47], the solvent changed [37], different dehydration modes of the parent hydrates utilized [37], etc. The preparation of isomeric forms is usually highly dependent on the precisely determined preparative conditions.

Complexes (6) and (7) have [47] very similar crystal structures with tetragonal CuN_4O_2 chromophores and differ in the degree of axial Cu—OCN interaction. Likewise complexes (13) and (14) only differ by the distortion of the tetragonal CuN_4O_2 chromophore [22]. However, complex (15) isomeric with the former two complexes is crystallostructurally dissimilar and displays a pseudooctahedral $CuN_4^{eq}N_2^{ax}$ moiety [22]. A similar relationship as exists between isomers (13) and (15) also appears [59] between isomers (62) and (63). Since all the ligands involved exert some steric effect, it is probable that the effort to relieve the steric strain contributes to the stabilization of various isomeric forms.

In spite of their crystallographic similarity, complexes (54) and (55) differ in the symmetry of their coordination polyhedra [58], apparently in connection with differences in the Cu—N interatomic distances.

In the family of urotropine complexes [37] fine structural distinctions were revealed between the five-coordinated complexes (76) and (77), as well as between the pseudotetrahedral complexes (78) and (79), showing varying degrees of distortion (flattening). On the other hand, isomers (74) and (75) apparently are distinguished by a different coordination geometry (see Section G, (iv)). All these differences are most probably associated with different packing of the polymeric chains, with the arrangement of the hydrogen bonds or with the situation of the urt molecules in the crystal structure.

In complexes (81), (83) and (85) the $[Cu(NCO)_4]^{2-}$ anion displays [63,64] a distorted tetrahedral geometry, while in complexes (82) and (84) it has a square planar (or pseudooctahedral) arrangement. Chughtai and Keller showed [64] that the nature of the cation, particularly its symmetry and size, is one of the external factors influencing the stabilization of the anion in the given configuration.

Complex (90) probably has [69] basically the same dimeric structure as form (89) (see Section F), but a somewhat different hydrogen-bonding contact as a result of a different packing of Cu^{II} dimers and Bph_4^- anions.

The occurrence of stereo-bonding isomers is characteristic for cyanato—copper(II) complexes and thus it contributes to the verification and generalization of the concept [87] concerning the plasticity of the Cu^{II} coordination sphere.

J. REACTIVITY OF THE NCO GROUP COORDINATED TO THE Cu^{II} ATOM

Many cases are reported in the literature [108] showing that coordination of ligands to the central atom can change their chemical properties to such an extent that various chemical reactions can occur. The NCO group, coordinated to the Cu^{II} atom, is able to enter some reactions with other organic nitrogen ligands, which are coordinated to the same Cu^{II} atom. In these reactions new ligands are formed, being chelate bonded in the Cu^{II} complexes isolated. In some cases it is possible to release them from the respective complexes. Such reactions do not usually occur and it seems possible that their occurrence in the Cu^{II} coordination sphere is favoured by its plasticity [87], allowing a relatively large variability of Cu—ligand bond strengths.

As confirmed by X-ray crystallography [109], reaction of Cu^{II} with NCO^- and 3,5-dmpz forms nearly planar species, in which two 3,5-dimethyl-1-car-

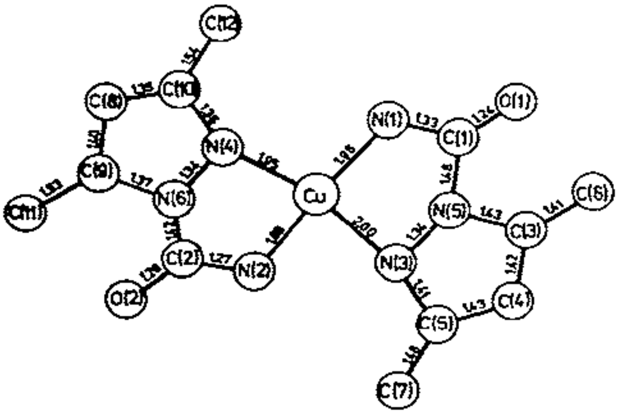


Fig. 12. Structural unit of α-Cu(3,5-dimethyl-1-carbamylpyrazolate)$_2$. Bond lengths in Å. After ref. 109.

bamylpyrazolate anions are coordinated to the Cu^{II} atom (Fig. 12). This new ligand apparently originates from a nucleophilic addition of the 3,5-dmpz molecule to the NCO group, connected with the transfer of the imino-hydrogen to the nitrogen of this group. The Cu^{II}-dmpz · NCO system is distinguishable from that of Cu^{II}—NCO by IR spectroscopy. The ν_{as}(NCO) band is shifted from its usual position of ca. 2200 cm^{-1} to ca. 1700 cm^{-1}, because the bonds in the bent NCO skeleton are double bond in character. In addition a strong band appears at ca. 1215 cm^{-1}, corresponding to the stretching vibration of the new C—N linkage, essentially single bond in character.

Cu^{II} reacts in the same way with NCO^- and pz, producing a Cu^{II} complex [58] containing two 1-carbamylpyrazolate anions as new ligands. The circumstances in this system are, however, more complicated, since according to the reaction conditions either the above complex or the cyanato complex $Cu(NCO)_2(pz)_2$ is obtained. The 1-carbamylpyrazole as well as its 3,5-dimethyl derivative can be released [110] from the respective complexes in water suspensions by the action of H_2S.

Copper(II) yields with NCO^- and ophda a product of the composition $Cu(NCO)_2$ · ophda · H_2O [61], exhibiting the ν_{as}(NCO) bands at ca. 1400 and 1370 cm^{-1}, which indicates a greater decrease of the C—N bond order in the NCO skeleton than in the former cases. Clearly there is a reaction between the NCO group and the ophda molecule and the new ligand forms a very stable chelate with the Cu^{II} atom.

Analogous reactions were not observed [110] in the case of the NCS group as ligand, nor with other metal atoms, such as Ni^{II}, Co^{II} and Zn^{II} as central atom.

K. CONCLUDING REMARKS

This review deals with copper(II) complexes containing NCO groups and organic nitrogen molecules as ligands. Hitherto about 110 complexes of this kind have been prepared and based on the experience gained, the preparation of further, purposefully selected complexes may be expected in the near future, because of their theoretical attraction and supposed applied importance.

Using direct and especially indirect methods of structure identification the coordination numbers ascertained for the Cu^{II} atom in cyanato—copper(II) complexes are four, five or six. The coordination polyhedra can be of pseudooctahedral, coplanar, pseudotetrahedral, tetragonal pyramidal or trigonal bipyramidal geometry, being influenced by the properties of ligands and by the effects of crystal structure packing. There also occur intermediate configurations between pseudooctahedral and coplanar, pseudotetrahedral and coplanar (or pseudooctahedral), as well as between tetragonal pyramidal and trigonal bipyramidal configurations. Also the existence of distortion isomers, conditioned by the plastic character of the Cu^{II} coordination sphere, is associated with this fact.

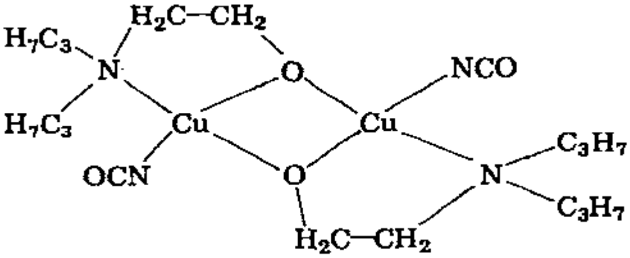
The cyanate group in all Cu^{II} complexes (perhaps with one exception [41]) is coordinated by the nitrogen atom; for bridging NCO groups the one-end N-bonding appears to be characteristic. In pseudooctahedral systems, however, it can form pseudobridges, in which, according to the conditions, either the equatorially bonded nitrogen atom or the free oxygen atom is involved. This fact causes in some cases the occurrence of stereo-bonding isomers [22, 59].

If the cyanate group is coordinated to the Cu^{II} atom simultaneously with an appropriate binitrogen ligand, a chemical reaction may take place between them with formation of a new ligand chelate bonded to the Cu^{II} atom [58, 109]. This phenomenon is probably connected with a specific influence of the Cu^{II} coordination sphere.

NOTE ADDED IN PROOF

After completion of this review, X-ray crystallographic results on a series of cyanato(2-dialkylaminoethanolato)copper(II), $Cu(NCO)\{R_2N(CH_2)_2O\}$ complexes, where $R = CH_3$ [111], n-C_4H_9 [112], n-C_3H_7 [113] and C_2H_5 [114], were reported. The complex with $R = C_3H_7$ was obtained in two isomeric modifications. Remarkable magnetic properties were discovered for some of the above compounds.

The crystal structures of these compounds * contain tetrameric, cubane-like oxygen bridged clusters with a Cu_4O_4 core, not previously observed for the Cu^{II}—NCO systems. The Cu^{II} atom environment is O_2O(apical)N(amino)N(NCO) ($R = CH_3$) or O(chelate)OO′N(amino)N(NCO) ($R = C_2H_5, C_3H_7, C_4H_9$). The coordination geometries are distorted square pyramidal ($R = CH_3$), between square pyramidal and trigonal bipyramidal ($R = C_2H_5, C_4H_9$) or distorted trigonal bipyramidal ($R = C_3H_7$). The monoclinic modification of $Cu(NCO)\{(C_3H_7)_2N(CH_2)_2O\}$ consists [113] of centrosymmetric, binuclear oxygen bridged units, exhibiting a distorted square planar stereochemistry.



The modifications with $R = C_3H_7$ differ significantly in their magnetic properties [113]. The magnetic moment of the binuclear compound is 0.72 B.M.

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* In the case of $R = C_3H_7$ an orthorhombic modification is considered.

at 298 K and decreases to zero at liquid nitrogen temperature; the Bleaney—Bowers model [80] yields $2J = -670$ cm^{-1}. On the other hand, the μ_{eff} value of the tetrameric compound is 1.89 B.M. at 298 K and decreases only to 1.46 B.M. at 78 K. The magnetic susceptibility of the complex with $R = C_2H_5$ [114], measured down to 2.6 K, has been fitted to the isotropic Heisenberg—Dirac—van Vleck model [115], J values of -21.4 cm^{-1} and $+12.3$ cm^{-1} having been obtained for the in-plane and out-of-plane exchange interaction, respectively.

Lastly McFadyen et al. [116] prepared a binuclear complex $Cu_2(NCO)R$, where R is a trianionic ligand derived from 4-hydroxy-bis-3,5-[N-(S-methyldithiocarbamate)formimidoyl]toluene. This complex is strongly antiferromagnetic, with a μ_{eff} value declining from 0.80 B.M. at 290 K to 0.40 B.M. at 99 K.

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