

NEW UNEXPECTED COORDINATION MODES OF AZIDE
AND PICOLINATO ANIONS ACTING AS BRIDGING LIGANDS
BETWEEN COPPER(II) AND SODIUM OR POTASSIUM
IONS. SYNTHESIS, CRYSTAL STRUCTURES AND SPECTRAL
CHARACTERIZATIONS OF $[\text{MCu}(\text{picolinato})(\text{N}_3)_2]_n$
(M = Na or K) COMPLEXES

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Abstract—The polymeric complexes $[\text{NaCu}(\text{picolinato})(\text{N}_3)_2]_n$ (1) and $[\text{KCu}(\text{picolinato})(\text{N}_3)_2]_n$ (2) have been synthesized and characterized by spectroscopic methods and X-ray crystallography. The overall spectral results indicate that the complexes contain different asymmetric azido ligands and axial five-coordinate copper(II) environments. In the structure of complex 1, each copper atom, which is chelated by O(1) and N(1) of the picolinato anion, links N(11), N(21) and N(21a) of the azido groups [Cu—O = 1.997(5) Å and Cu—N = 1.957(6)–2.488(6) Å]. Each sodium atom is six-coordinated to oxygen atoms O(1), O(2c) and O(2d) [Na—O = 2.299(6)–2.470(6) Å] of picolinato ligand and nitrogen atoms N(11), N(11a), N(13e) [Na—N = 2.454(7)–2.686(7) Å] of azide groups. Both $\mu(1,1)$ and $\mu(1,1,1,3)$ bridging azido ligands are linear and asymmetric [N(11)—N(12) = 1.204(8), N(12)—N(13) = 1.137(8), N(21)—N(22) = 1.204(8), N(22)—N(23) = 1.152(10) Å]. The structure of polymeric complex 2 features five-coordinate copper(II), eight-coordinate potassium, $\mu(1,3)$ and $\mu(1,1,1,3,3)$ bridging azido ligands and *O,O,O',O',O'*, *N*-hexadentate picolinato anions. The Cu—O bond length is 1.990(3) Å, Cu—N distances from 1.930(3) to 2.649(4) Å, whereas the K—O distances are 2.729(3)–3.081(3) Å and K—N 2.845(4)–3.289(5) Å.

The azide ion, N_3^- , is a versatile ligand which can function as a terminal mono-dentate^{1–5} or bridging bi-, tri- and tetra-dentate ligand. In the case of bridging bi-dentate, the coordination modes $\mu(1,1)$,^{6,7} di- $\mu(1,1)$,^{8–11} $\mu(1,3)$ ^{12–14} and di- $\mu(1,3)$ ^{15–19} have been observed, whereas in the case of bridging

tri-dentate $\mu(1,1,1)$ ^{20,21} and $\mu(1,1,3)$ ^{20,22} have been found. In contrast, both bridging types of tetra-dentate azido ligands, $\mu(1,1,3,3)$ and $\mu(1,1,1,3)$, are very scarce and uniquely exemplified in α - $[\text{Pb}(\text{N}_3)_2]_\infty$,²³ a compound whose structure was determined by the neutron diffraction method.

Recently, we used the azide ion to isolate and characterize what appears as a new class of complexes containing two different metal atom centres,

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an alkali metal atom centre and a transition metal atom centre, connected together by azide ligands. Of this class of complexes we isolated $\text{MCr}(\text{pyridine})_n(\text{N}_3)_4$ ($n = 4$ for $\text{M} = \text{Na}$ or K , and $n = 3$ for Rb),^{24,25} $\text{NaMn}(\text{pyrazinato})(\text{N}_3)_2(\text{H}_2\text{O})_2$,²⁶ and in a previous paper we described the structure of $\text{NaCu}(\text{picolinato})_2(\text{N}_3)(\text{H}_2\text{O})_2$,²⁷ the first example of picolinic acid complexes containing *N,O,O',O'*-penta-dentate chelating bridging picolinato anions. This latter complex was deposited along with grass-green fine crystals of another copper(II) azide complex of picolinic acid. Now, we have succeeded in synthesizing suitable crystals of the green complex along with the corresponding potassium complex for which the general formula is $\text{MCu}(\text{picolinato})(\text{N}_3)_2$. The structural characterizations of these new anhydrous green complexes elucidated by spectroscopic and X-ray diffraction methods are the subject of the present study.

EXPERIMENTAL

Picolinic acid was obtained from Aldrich and other chemicals are of analytical grade quality.

Preparation of $[\text{NaCu}(\text{picolinato})(\text{N}_3)_2]_n$ (1)

Copper(II) nitrate trihydrate (0.48 g, *ca* 2 mmol) dissolved in 10 cm³ ethanol and picolinic acid (0.25 g, *ca* 2 mmol) in 40 cm³ ethanol were mixed together. To this mixture a dilute solution of NaN_3 (0.26 g, 4 mmol, in 5 cm³ water) was added dropwise and the solution shaken thoroughly after each addition until a deep green coloured solution was obtained. If a green precipitate formed after several minutes the mixture should be filtered off. To the green filtrate an excess of NaN_3 solution was added and the final mixture allowed to stand in an open beaker in a normal temperature over several days until well-formed grass-green crystals of the complex deposited. Found: C, 24.8; H, 1.5; N, 33.4; Cu, 21.8. Calc.: C, 24.6; H, 1.4; N, 33.5; Cu, 21.7%.

Preparation of $[\text{KCu}(\text{picolinato})(\text{N}_3)_2]_n$ (2)

To an aqueous/ethanolic solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (3 mmol) and picolinic acid (3 mmol), an aqueous solution of KN_3 (5 mmol) was added dropwise with constant stirring and the solution was filtered off. To the green filtrate two drops of azide solution were added and the solution was left undisturbed for several days. Dark green crystals of the complex were collected, filtered and washed with the mother liquor. Found: C, 23.1; H,

1.4; N, 31.4; Cu, 20.8. Calc.: C, 23.3; H, 1.3; N, 31.8; Cu, 20.6%.

The experimental procedures and instruments used for other physical measurements are as described previously.²⁵

X-ray crystallography

A modified STOE four-circle diffractometer was used for single crystal X-ray measurements. Lattice parameters were obtained by least-squares refinement of the diffraction data from 50 (compound 1) and 25 (compound 2) reflections in the 2θ range 8–25°. Data were collected at 296(1) K using graphite crystal-monochromatized Mo- K_α radiation ($\lambda = 0.71069$ Å) and the ω -scan technique. The intensities were corrected for Lorentz and polarization effects, and for absorption by an empirical method. Crystallographic data are given in Table 1.

The structures were solved by Patterson methods. Anisotropic displacement parameters were only applied to the non-hydrogen atoms in full-matrix least-squares refinements. The hydrogen atoms were included in the final refinement cycles on calculated positions. The programs DIFABS,²⁸ SHELX-76,²⁹ SHELXS-86,³⁰ PLATON³¹ and THE XRAY SYSTEM³² were used for computations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.³³ Selected bond distances and bond angles are given in Table 2. Positional parameters, anisotropic displacement parameters, hydrogen atom coordinates, a full list of bond lengths and angles and observed and calculated structure factors have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

The interaction between copper(II) ions and picolinic acid in an ethanolic medium in the presence of sodium azide afforded two different complexes: a blue complex formulated as $\text{NaCu}(\text{picolinato})_2(\text{N}_3)(\text{H}_2\text{O})_2$ and described previously,²⁷ and the grass-green complex 1 having the formula $\text{NaCu}(\text{picolinato})(\text{N}_3)_2$. The isolation of one or the other of these two complexes depends on the relative molar ratio of picolinic acid and azide ion in the reaction mixture. In the case of potassium azide we could not isolate the hydrated form. Figures 1 and 2 illustrate the principle structural features of complex 1. The picolinato anion chelates a copper atom through its oxygen atom O(1) and nitrogen atom N(1) [$\text{Cu}-\text{O}(1) = 1.997(5)$ Å and $\text{Cu}-\text{N}(1) = 2.012(5)$ Å]. Each five-coordinate cop-

Table 1. Crystallographic data and processing parameters for compounds **1** and **2**

Compound	1	2
Molecular formula	C ₆ H ₄ CuNaN ₇ O ₂	C ₆ H ₄ CuKN ₇ O ₂
Molecular weight	292.68	308.79
Crystal system	Triclinic	Triclinic
<i>a</i> (Å)	3.561(1)	3.796(2)
<i>b</i> (Å)	9.984(3)	10.271(4)
<i>c</i> (Å)	13.659(6)	13.185(5)
α (°)	100.19(3)	100.73(3)
β (°)	94.58(3)	98.00(3)
γ (°)	90.33(2)	94.79(3)
<i>V</i> (Å ³)	476.3(3)	497.0(4)
Space group	<i>P</i> −1 (No. 2)	<i>P</i> −1 (No. 2)
<i>Z</i>	2	2
<i>F</i> (000)	290	306
μ (Mo- <i>K</i> _α) (mm ^{−1})	2.34	2.62
<i>D</i> _{calc} / <i>D</i> _{obs} (Mg m ^{−3})	2.040/2.03(2)	2.063/2.05(2)
Approx. crystal size (mm)	0.85 × 0.30 × 0.10	0.65 × 0.12 × 0.08
Data collection limits	± <i>h</i> , ± <i>k</i> , <i>l</i> ; 2 θ < 55°	± <i>h</i> , ± <i>k</i> , <i>l</i> ; 2 θ < 52°
Scan mode	ω -scan, $\Delta\omega$ = 1.50°	ω -scan, $\Delta\omega$ = 1.50°
<i>I</i> > 4 σ (<i>I</i>)	2113	1582
Least-squares parameters	158	158
<i>R</i>	0.079	0.030
<i>R</i> _w	0.082	0.033
Weighting scheme	9.638 σ ^{−2} (<i>F</i> _o)	0.564 σ ^{−2} (<i>F</i> _o)
Residual extrema in final difference map (e Å ^{−3})	+1.1/−1.3	+0.6/−0.3

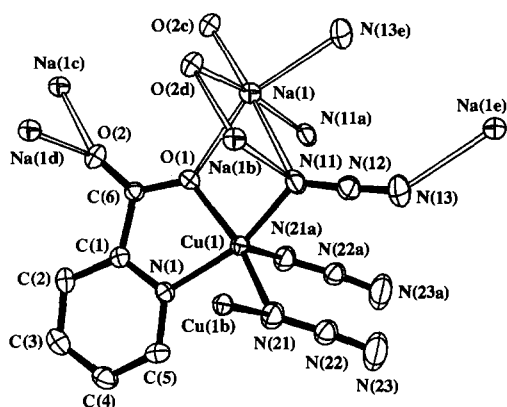


Fig. 1. Atom numbering scheme of [NaCu(picolinato)(N₃)₂]_n (**1**). Symmetry code according to Table 2.

per atom further binds the nitrogen atoms N(11), N(21) and N(21a) [Cu—N = 1.957(6)–2.488(6) Å] of the azido ligands. The sodium atom centre, on the other hand, links the oxygen atoms O(1), O(2c) and O(2d) of picolinato anions at Na—O distances from 2.299(6) to 2.470(6) Å, and nitrogen atoms N(11), N(11a) and N(13e) [Na—N = 2.454(7)–2.686(7) Å] of the azido ligands, giving rise to an NaO₃N₃ distorted octahedron. Both azido ligands

were almost linear and asymmetric [N(11)—N(12) = 1.204(8), N(12)—N(13) = 1.137(8) Å, N(21)—N(22) = 1.204(8), N(22)—N(23) = 1.152(10) Å]. The Na—N distances found in the present structure are longer than the corresponding values found in NaCu(picolinato)₂(N₃)(H₂O)₂ (**3**) [2.388(4) Å]²⁷ and NaMn(pyrazinato)(N₃)₂(H₂O)₃ (**4**) [Na—N = 2.415(4)–2.517(4) Å],²⁶ but are close to those (2.61–2.64 Å) found in other NaN₆ coordination octahedra.³⁴ The Na—O bond lengths (Table 2) match very well with the corresponding values found in **4** [2.355(3)–2.750(3) Å] and other sodium complexes (2.32–2.97 Å).^{35,36}

The most noticeable feature of the present structure is the penta-dentate coordination mode of the bridging mode of the picolinato anion, as well as the occurrence of the μ (1,1,1,3) bridging mode by the azido ligand N(11)—N(12)—N(13) (Fig. 1). To our knowledge each of the penta-dentate picolinato anion and μ (1,1,1,3) azido ligand has been observed only once in the structures of NaCu(picolinato)₂(N₃)(H₂O)₂ (**3**)²⁷ and α -[Pb(N₃)₂]_∞,²³ respectively. Neutron diffraction study of α -[Pb(N₃)₂]_∞ has shown that the compound contains two types of tetra-dentate azido ligands, μ (1,1,3,3) and μ (1,1,1,3) bridges. The N—N bond distances within the μ (1,1,1,3) azide group of N(1)—

Table 2. Selected bond distances (Å) and bond angles (°) for complexes **1** and **2**

[NaCu(picolinato)(N ₃) ₂] _n (1)			
Cu(1)—N(21)	1.981(6)	Cu(1)—N(21a)	2.488(6)
Na(1)—O(1)	2.351(5)	Na(1)—N(11)	2.528(7)
Na(1) . . . Na(1a)	3.561(4)	Na(1)—N(11a)	2.686(7)
Na(1) . . . Na(1b)	3.561(4)	Na(1)—O(2c)	2.299(6)
Na(1)—O(2d)	2.470(6)	Na(1)—N(13e)	2.454(7)
O(1)—C(6)	1.275(7)	O(2)—C(6)	1.224(8)
N(11)—N(12)	1.204(8)	N(12)—N(13)	1.137(8)
N(21)—N(22)	1.204(8)	N(22)—N(23)	1.152(10)
O(1)—Cu(1)—N(1)	79.9(2)	O(1)—Cu(1)—N(21a)	89.8(2)
O(1)—Cu(1)—N(11)	86.2(2)	O(1)—Cu(1)—N(21)	163.7(2)
N(1)—Cu(1)—N(11)	163.0(2)	N(1)—Cu(1)—N(21a)	92.1(2)
N(1)—Cu(1)—N(21)	92.8(2)	N(11)—Cu(1)—N(21a)	97.6(2)
N(11)—Cu(1)—N(21)	98.0(3)	N(21)—Cu(1)—N(21a)	105.1(2)
Cu(1)—O(1)—Na(1)	105.1(2)	Cu(1)—N(11)—N(12)	126.4(5)
N(11)—N(12)—N(13)	176.5(7)	Cu(1)—N(21)—N(22)	122.8(5)
Cu(1)—N(21)—Cu(1b)	105.1(3)	N(22)—N(21)—Cu(1b)	117.7(5)
N(21)—N(22)—N(23)	175.7(8)	O(1)—C(6)—O(2)	127.3(6)
[KCu(picolinato)(N ₃) ₂] _n (2)			
Cu(1) . . . K(1)	3.955(2)	Cu(1)—O(1)	1.990(3)
Cu(1)—N(1)	2.003(3)	Cu(1)—N(11)	1.949(4)
Cu(1)—N(21)	1.930(3)	Cu(1)—N(11b)	2.649(4)
K(1)—O(1)	2.849(3)	K(1)—N(11)	2.973(4)
K(1)—O(1a)	3.081(3)	K(1)—N(13c)	2.845(4)
K(1)—N(13d)	2.892(4)	K(1)—N(23d)	3.289(5)
K(1)—O(2e)	2.729(3)	K(1)—O(2f)	2.729(3)
O(1)—C(6)	1.260(4)	O(2)—C(6)	1.235(4)
N(11)—N(12)	1.195(4)	N(12)—N(13)	1.141(5)
N(21)—N(22)	1.194(5)	N(22)—N(23)	1.141(5)
O(1)—Cu(1)—N(1)	81.1(1)	O(1)—Cu(1)—N(11)	89.1(1)
O(1)—Cu(1)—N(21)	171.9(2)	O(1)—Cu(1)—N(11b)	84.6(1)
N(1)—Cu(1)—N(11)	157.0(1)	N(1)—Cu(1)—N(21)	91.3(1)
N(1)—Cu(1)—N(11b)	89.5(1)	N(11)—Cu(1)—N(21)	99.0(1)
N(11)—Cu(1)—N(11b)	110.4(1)	N(21)—Cu(1)—N(11b)	92.6(1)
Cu(1)—N(11)—N(12)	125.0(3)	Cu(1)—N(11)—Cu(1a)	110.4(1)
N(12)—N(11)—Cu(1a)	100.2(2)	N(11)—N(12)—N(13)	176.6(4)
Cu(1)—N(21)—N(22)	128.5(3)	N(21)—N(22)—N(23)	175.0(5)
O(1)—C(6)—O(2)	125.6(3)		

Symmetry code for complex **1**: (a) $x-1, y, z$; (b) $x+1, y, z$; (c) $-x-1, -y, 1-z$; (d) $-x, -y, 1-z$; (e) $-x, 1-y, 1-z$.

Symmetry code for complex **2**: (a) $x-1, y, z$; (b) $x+1, y, z$; (c) $-x-1, -y, 1-z$; (d) $-x, -y, 1-z$; (e) $-x, 1-y, 1-z$; (f) $1-x, 1-y, 1-z$.

N(2) = 1.213(10) and N(2)—N(3) = 1.147(13) Å match very well with the corresponding values found in the present complex for N(11)—N(12)—N(13). The degrees of asymmetry Δd (Δd is the difference between the two N—N distances within an azido group) of 0.046 and 0.067 Å found for $\mu(1,1,1,3)$ azido ligands in polymeric α -[Pb(N₃)₂]_∞ and complex **1**, respectively, are comparable with that (0.052 Å) found in the structure of RbCr(pyridine)₃(N₃)₄, but greater than the Δd of 0.021 Å in the structure of Cu(DENA)(N₃)₂²² (DENA = diethylnicotinamide), both containing

$\mu(1,1,3)$ bridging azido ligands. End-on tri-dentate, or end-on triply bridging azide coordination, $\mu(1,1,1)$, has been observed only twice in the polymeric structures of [Cu(N₃)₂]_n featuring independent azido groups, in one of which an end nitrogen atom symmetrically bridges two metal atoms [2.003(4) Å × 2] and forms a further long bond of 2.709(7) Å with a third,²⁰ and Cu₃(benzoylpyridine)₂(N₃)₆.²¹

The structure of complex **1** differs significantly from that of complex **4** also containing two azido groups and a single pyrazinato anion. Complex **4**

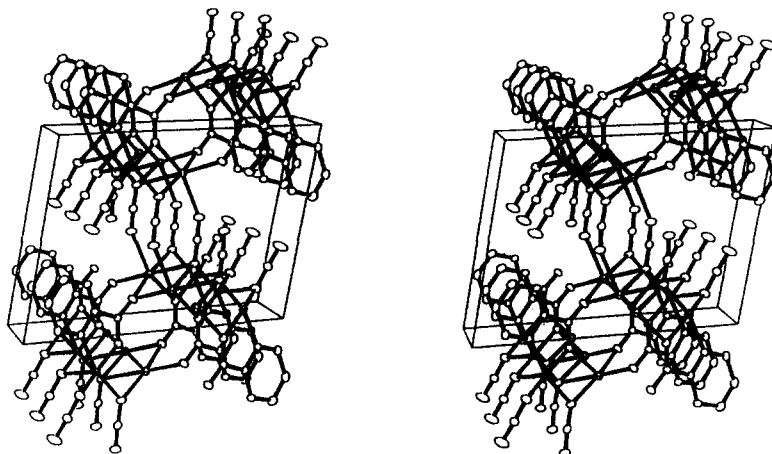


Fig. 2. Packing of $[\text{NaCu}(\text{picolinato})(\text{N}_3)_2]_n$ (1), viewed along the a -axis of unit cell.

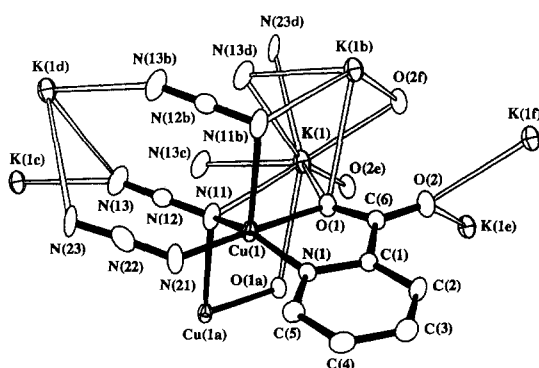


Fig. 3. Atom numbering scheme of $[\text{KCu}(\text{picolinato})(\text{N}_3)_2]_n$ (2). Symmetry code according to Table 2.

crystallizes with two aqua ligands and the pyrazinato anion functions only as a chelating N,O -bidentate ligand as compared to the penta-dentate picolinate anion in complex 1. Complex 4 features octahedrally coordinated manganese and sodium

atoms, $\mu(1,1,3)$ bridging azido ligands, bridging and terminally bonded aqua molecules and a hetero dinuclear unit, $\text{Na}-\mu(\text{N}_3)-\mu(\text{OH}_2)-\text{Mn}$. The two $\mu(1,1,3)$ bridging azido ligands in complex 4, having great difference in their degrees of asymmetry ($\Delta d = 0.014 \text{ \AA}$ for one azide and 0.058 \AA for the other; (Table 2 and ref. 27) are more symmetrical than the $\mu(1,1,1,3)$ azido ligand in the structure of complex 1.

In the structure of complex 2, although the lattice parameters, packing of polyhedra and coordination environment of copper(II) are very similar to those in the structure of 1, differences occur in the coordination environments around potassium and coordination modes of the two azido groups and picolinato anions. As can be seen in Figs 3 and 4, the oxygen atom O(1) of the picolinato anion binds one copper(II) atom and two potassium atoms, whereas the oxygen atom O(2) links two different potassium atoms. As the copper(II) atom is also bonded to the heterocyclic N(1), the picolinato

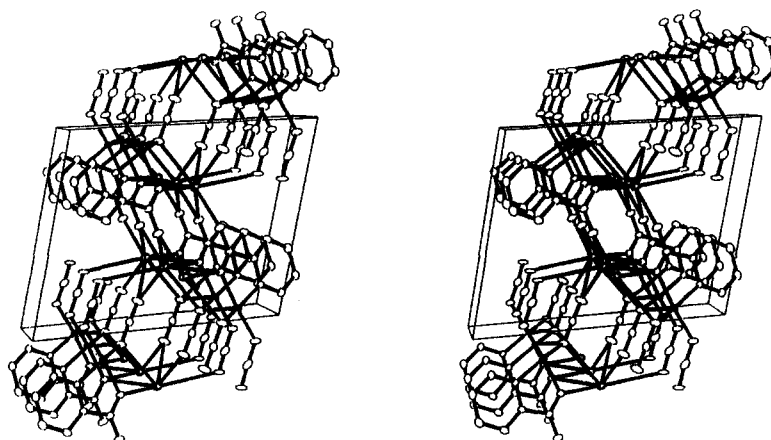


Fig. 4. Packing of $[\text{KCu}(\text{picolinato})(\text{N}_3)_2]_n$ (2), viewed along the a -axis of unit cell.

groups therefore function as a chelating bridging O,O,O',O',O',N -hexa-dentate ligand. The azide group $N(11)-N(12)-N(13)$ binds two copper(II) atoms and one potassium atom at $N(11)$ and two different potassium atoms at $N(13)$, thus behaving as a $\mu(1,1,1,3,3)$ bridging penta-dentate ligand, whereas $N(21)-N(22)-N(23)$ links a copper atom at one end and a potassium atom at the other end in $\mu(1,3)$ fashion. Each eight-coordinated potassium atom binds $O(1)$, $O(1a)$, $O(2e)$ and $O(2f)$ from picolinato anions and $N(11)$, $N(13c)$, $N(13d)$ and $N(23d)$ from azido ligands, giving rise to a distorted antiprismatic geometry. This is the first time these different types of coordinating modes of both picolinato anion and azido ligand have been reported in picolinic acid or metal azido complexes.

The IR spectral data for free picolinic acid and its complexes are collected in Table 3. The spectrum of complex **1** exhibits two very strong bands at 1675 and 1650 cm^{-1} due to the $\nu_{\text{as}}(\text{COO})$ mode, in addition to a very strong band at 1380 cm^{-1} associated with the $\nu_{\text{s}}(\text{COO})$ mode. The corresponding bands for complex **2** appear at 1684, 1650, 1636 and 1384 cm^{-1} . The appearance of two $\nu_{\text{as}}(\text{COO})$ bands is consistent with the fact that the picolinato anion contains two significantly different

C—O bond distances in both complexes. Their positions, however, are higher than those found for other penta-dentate picolinato anions in complex **4**. The crystal structure determinations show that Δd values of the two azido ligands in both complexes **1** and **2** are little different, although they function differently in each complex. Accordingly, one expects two absorption bands associated with each $\nu_{\text{as}}(\text{N}_3)$ mode. While the results given in Table 3 confirm this prediction, the positions of the $\nu_{\text{as}}(\text{N}_3)$ band are not consistent with the Δd vs $\nu_{\text{as}}(\text{N}_3)$ relationship reported earlier.^{37,38} According to this relationship the two azido groups $N(11)-N(12)-N(13)$ ($\Delta d = 0.067 \text{ \AA}$) and $N(21)-N(22)-N(23)$ ($\Delta d = 0.052 \text{ \AA}$) in complex **1** are expected to show their $\nu_{\text{as}}(\text{N}_3)$ absorption bands around 2065 and 2046 cm^{-1} , respectively. Assuming that the lower frequency band at 2050 cm^{-1} is due to azide $N(21)-N(22)-N(23)$, the higher frequency 2125 cm^{-1} band appears at a much higher frequency than expected. The same is true for complex **2**. This result suggests that such a Δd vs $\nu_{\text{as}}(\text{N}_3)$ relationship should be viewed with caution. The appearance of absorption bands due to the $\nu_{\text{s}}(\text{N}_3)$ mode in the vicinity of 1300 cm^{-1} , however, is strong evidence of the asymmetric nature of the azido ligands in

Table 3. IR spectral data for complexes **1** and **2**

pic-H	[NaCu(pic)(N ₃) ₂] _n (1)	[KCu(pic)(N ₃) ₂] _n (2)	Assignments
2600 s,br	2125 vs	2128 vs	$\nu(\text{O}-\text{H} \cdots \text{O})$
	2055 vs	2050 s	$\nu_{\text{as}}(\text{N}_3)$
1715 s,br			$\nu(\text{C}=\text{O})$
1650 ms	1675 vs	1684 s	$\nu_{\text{as}}(\text{COO})$
	1655 vs	1650 ms 1636 m	
1595 vs	1600 s	1604 ms	pyridine
1573 s	1565 w	1570 w	
1529 m	1550 w	1550 w	
	1535 w	1540 w	
1455 s	1475 m	1480 m	
1307 vs	1380 vs,br	1384 vs	$\nu_{\text{s}}(\text{COO})$
	1340 m	1335 m	$\nu_{\text{s}}(\text{N}_3)$
1085 m	1090* m	1085 m	pyridine
1010 ms	1025 ms	1025 ms	
	365 m	370 ms	$\nu[\text{Cu}-\text{N}(\text{N}_3)]$
	340 m	350 ms	
	315 m	310 m	$\nu[\text{Cu}-\text{O}(\text{pic})]$
260 vs	290 m	285 m	pyridine + $\nu[\text{Cu}-\text{O}(\text{pic})]$
	260 s	268 s	$\nu[\text{Cu}-\text{N}(\text{pic})]$
	230 vs	240 s	

s = strong, m = medium, w = weak, v = very, br = broad; asterisk denotes a split broadened band; pic = picolinato.

both complexes. The tentative assignments of the metal–ligand vibrations in the far-IR spectral region for both complexes are given in accordance with ref. 39.

The electronic spectra of the title complexes (Fig. 5) measured as solids mullied in Nujol exhibit *d-d* transitions as a broad band centred around 15,150 and 14,900 cm^{-1} for **1** and **2**, respectively, suggesting five-coordinate copper(II) environments^{40,41} for both complexes. The spectrum of **1** also shows two very strong absorption bands at 24,600 and 27,000 cm^{-1} . The corresponding absorption bands for **2** appear at 24,100 and 26,600 cm^{-1} , along with a pronounced shoulder at *ca* 20,408 cm^{-1} . The bands are due to $\text{N}_3^- \rightarrow \text{Cu}^{\text{II}}$ charge-transfer transitions. A recent study using the transition dipole vector model predicts two azide-to-copper(II) charge transfers for a terminal azide, whereas four such transitions are expected when the azide bridges two copper(II) atoms in either μ -1,3 or μ -1,1 geometry.⁴² However, for terminal copper(II) azide monomers only one feature is observed, π_{σ}^{nb} -to-copper(II) charge transfer, whereas two bands are observed for μ -1,3 or μ -1,1 dimers.⁴² The present structures contain two azido ligands, one which bridges two copper atoms and another which bridges one copper atom with other different alkali metal atoms, thus acting as a terminal group with respect to the copper atom. Therefore, we expect three azide-to-copper charge-transfer bands to be observed, as seen from Fig. 5. Since a distinct absorption band is usually observed in the region 17,000–21,000 cm^{-1} for copper(II) complexes con-

taining $\mu(1,1)$ azides, the band at 20,408 cm^{-1} is evidently due to the $\mu(1,1)$ azide-to-copper charge-transfer transitions.

The powder ESR spectra at room temperature of the title complexes are of the axial type with $g_{\parallel} = 2.248$ and 2.230 and $g_{\perp} = 2.065$ and 2.042 for **1** and **2**, respectively. This result is consistent with the room-temperature magnetic moment values of 1.82 B.M. (**1**) and 1.86 B.M. (**2**). This is in keeping with magnetically diluted tetragonal copper(II) systems showing an orbitally non-degenerate ground state.⁴³

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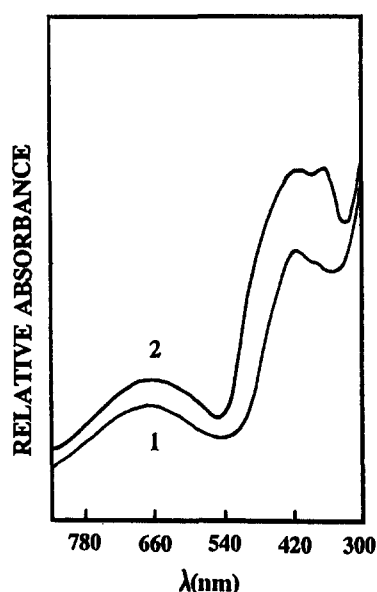


Fig. 5. Reflectance spectra of solid complexes: **1**, $[\text{NaCu}(\text{picolinate})(\text{N}_3)_2]_n$; **2**, $[\text{KCu}(\text{picolinate})(\text{N}_3)_2]_n$.

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