Fig. 1. ORTEP (Johnson, 1965) drawing of a section of the linear-chain anion with thermal ellipsoids at the 50% probability level. Mn(1) lies on a inversion center, Mn(2) on a twofold axis approximately perpendicular to the plane of the drawing.

by difference Fourier synthesis and included in the refinement with isotropic temperature factors. Anisotropic temperature factors used for the heavier atoms. Atomic scattering factors for neutral atoms from Cromer & Mann (1968), corrections for anomalous dispersion from Cromer & Liberman (1970). Final $R = 0.042$, $wR = 0.036$ with weights $w = 1/\sigma^2(F_o)$ for the 833 observed reflections.* $(\Delta/\sigma)_{max} = 0.005$, $\Delta\rho_{max,min} = 0.33$, -0.35 e Å^{-3}. The final atomic parameters are given in Table 1, and interatomic distances and angles are given in Table 2. Fig. 1 shows a section of the infinite linear-chain anions, Fig. 2 the orientation of the chains in the cell and the positions of the K cations.

Related literature. The isotypic structure of Rb[MnF$_4$(H$_2$O)] was determined by Kaučič & Bukovec (1979). Magnetic studies on the Rb and K compounds have been published by Massa & Pebler (1986), Palacio, Andres, Horne & van Duynefeldt (1986), Nuñez, Darriet, Bukovec, Tressaud & Hagenmuller (1987) and Pebler, Massa, Lass & Ziegler (1987).

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44397 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
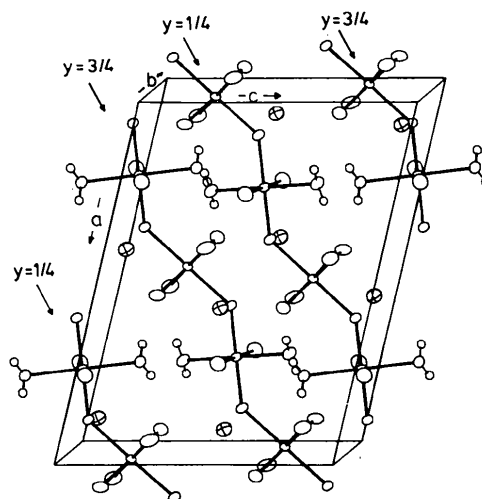

Fig. 2. View of the unit-cell contents illustrating the chain packing.

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Structure of a New Polymorph of Bis(μ-pyridine N-oxide)-bis[aquadichlorocopper(II)]

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Abstract. [Cu$_2$Cl$_4$(H$_2$O)$_2$(C$_5$H$_5$NO)$_2$], $M_r = 495.14$, monoclinic, $P2_1/c$, $a = 9.899$ (2), $b = 10.028$ (1), $c = 10.006$ (2) Å, $\beta = 117.20$ (1)°, $V = 883.5$ (2) Å^3, $Z = 2$, $D_x = 1.86$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 30.4$ cm^{-1}, $F(000) = 492$, $T = 299$ K, final $R = 0.034$ for 1056 reflections with $F_o \geq 3\sigma(F_o)$. The dimer

is centrosymmetric with bridging N-oxides. The Cu atom is five-coordinate, with Cu—Cl(1), 2·220 (1); Cu—Cl(2), 2·223 (2); Cu—OH$_2$, 2·266 (4); Cu—O(N-oxide), 2·010 (3) and 2·014 (3) Å. The corresponding distances in the two reports of the triclinic form are 2·215 (1), 2·220 (1), 2·336 (3), 1·995 (2), 2·014 (2) Å and 2·213 (1), 2·221 (1), 2·342 (4), 1·979 (4), 2·007 (4) Å.

Experimental. A mixture of 2,6-pyridinedicarboxylic acid (0·1831 g, 1·00 mmol) and copper chloride dihydrate (0·3410 g, 2·00 mmol) in 1-butanol (b.p. 390–391 K) was refluxed overnight. After cooling and slowly evaporating the solvent to a volume of about 10 mL, green crystals of the title compound, (1), suitable for an X-ray study were obtained. The X-ray data were measured using a Nicolet R3m diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. The crystal was 0·20 × 0·20 × 0·20 mm.

(1)
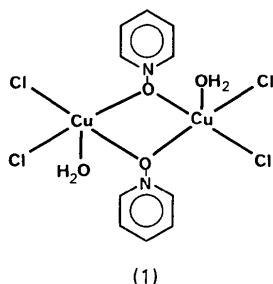
Cell constants were determined using 17 reflections in the 2θ range of 11·5 to 26·2°. A total of 1559 reflections in the 2θ range of 0 to 45° (h 0 to ±9, k 0 to 10, l 0 to 10) were measured. Two standard reflections measured after every 98 reflections showed a variation of ±3·5%. Absorption corrections were considered unnecessary because of the equidimensional shape of the crystal and the small value of μr. The 1057 reflections with $F_o \geq 3\sigma(F_o)$, $R_{int} = 0·015$, were used in the analysis. The structure was solved by Patterson and Fourier methods. The refinement of the 100 parameters was by least-squares method on F_o and minimized $\sum w(|F_o| - |F_c|)^2$. The H atoms were located in a difference Fourier synthesis and were included in the calculations with $U = U_{iso}$ for the attached atom + 0·025 Å^2 but were not refined. The $\overline{2}12$ reflection was given zero weight in the final refinement ($F_o = 156·9$, $F_c = 181·6$). The weights used were $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ where g was refined to a value of 0·00085. The final R was 0·034 and wR was 0·040 with the g.o.f. equal to 1·37. In the final difference Fourier synthesis $\Delta\rho_{max}$ was +0·38 and $\Delta\rho_{min}$ was −0·59 e Å^{-3}. $(\Delta/\sigma)_{max}$ = 0·01. All calculations were carried out using the SHELXTL program (Sheldrick, 1983), on an Eclipse Model 30 computer. Atomic scattering factors from SHELXTL. Atomic coordinates are listed in

Table 1 and bond distances and angles in Table 2.* A view of the model showing the atomic numbering and thermal ellipsoids is given in Fig. 1.

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* Tables of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44346 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *for* [Cu$_2$Cl$_4$-(H$_2$O)$_2$(C$_5$H$_5$NO)$_2$]

	x	y	z	U^*
Cu	60 (1)	8621 (1)	914 (1)	29 (1)
Cl(1)	−1337 (1)	6806 (1)	−35 (1)	41 (1)
Cl(2)	1966 (1)	7692 (1)	2896 (2)	52 (1)
O(1)	1245 (3)	10231 (3)	862 (3)	35 (1)
O(2w)	−1108 (4)	9562 (3)	2171 (4)	43 (2)
N(1)	2750 (4)	10400 (4)	1705 (4)	31 (2)
C(2)	3725 (6)	9820 (5)	1283 (6)	46 (2)
C(3)	5243 (5)	10012 (6)	2127 (7)	53 (2)
C(4)	5752 (5)	10763 (5)	3391 (6)	51 (2)
C(5)	4768 (6)	11339 (5)	3824 (6)	47 (2)
C(6)	3234 (5)	11156 (5)	2939 (5)	39 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Distances* (Å) *and angles* (°) *in* [Cu$_2$-Cl$_4$(H$_2$O)$_2$(C$_5$H$_5$NO)$_2$]

|			
Cu—Cl(1)	2·220 (1)	Cu—Cl(2)	2·223 (1)
Cu—O(1)	2·010 (3)	Cu—O(2w)	2·266 (4)
Cu—O(1^i)	2·014 (3)	O(1)—N(1)	1·346 (4)
O(1)—Cu^i	2·014 (3)	N(1)—C(2)	1·349 (8)
N(1)—C(6)	1·337 (6)	C(2)—C(3)	1·360 (7)
C(3)—C(4)	1·356 (8)	C(4)—C(5)	1·363 (9)
C(5)—C(6)	1·377 (6)		
Cl(1)—Cu—Cl(2)	98·4 (1)	Cl(1)—Cu—O(1)	154·7 (1)
Cl(2)—Cu—O(1)	95·3 (1)	Cl(1)—Cu—O(2w)	101·7 (1)
Cl(2)—Cu—O(2w)	96·9 (1)	O(1)—Cu—O(2w)	97·6 (1)
Cl(1)—Cu—O(1^i)	93·9 (1)	Cl(2)—Cu—O(1^i)	165·4 (1)
O(1)—Cu—O(1^i)	70·4 (1)	O(2w)—Cu—O(1^i)	88·2 (1)
Cu—O(1)—N(1)	125·3 (2)	Cu—O(1)—Cu^i	109·6 (1)
N(1)—O(1)—Cu^i	124·1 (3)	O(1)—N(1)—C(2)	119·6 (4)
O(1)—N(1)—C(6)	118·5 (4)	C(2)—N(1)—C(6)	121·9 (4)
N(1)—C(2)—C(3)	119·3 (5)	C(2)—C(3)—C(4)	119·5 (6)
C(3)—C(4)—C(5)	121·1 (4)	C(4)—C(5)—C(6)	118·5 (5)
N(1)—C(6)—C(5)	119·6 (5)		
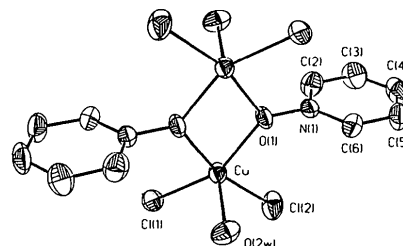
Fig. 1. A view of bis(μ-pyridine N-oxide)-bis[aquadichlorocopper(II)] showing the atomic numbering and 50% thermal ellipsoids. A center of symmetry is present between the Cu atoms.

Related literature. The structure of the triclinic form of [Cu$_2$Cl$_4$(H$_2$O)$_2$(pyridine N-oxide)$_2$] has been reported by both Estes & Hodgson (1976) and Paulson, Krost, McPherson, Rogers & Atwood (1980). The main differences in the three structures are the Cu—OH$_2$ and Cu—O(pyridine N-oxide) distances. A copper complex of the starting material 2,6-pyridinedicarboxylic acid has been prepared by Nathan, Doyle, Mooring, Zapren, Larsen & Pierpont (1985) but no structural study was reported.

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Structure of Bis(tetraphenylphosphonium) Tris[isothiocyanatocopper(I)]oxotrithiomolybdate(VI)*

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Abstract. [P(C$_6$H$_5$)$_4$]$_2$[MoOS$_3$\{Cu(NCS)\}$_3$], $Mr =$ 1251·8, triclinic, $P\bar{1}$, $a = 12\cdot480$ (2), $b = 12\cdot930$ (2), $c = 18\cdot646$ (2) Å, $\alpha = 83\cdot944$ (5), $\beta = 73\cdot177$ (6), $\gamma = 65\cdot188$ (6)°, $V = 2613\cdot8$ Å^3, $Z = 2$, $D_x =$ 1·590 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu =$ 1·77 mm^{-1}, $F(000) = 1260$, $T = 293$ K, $R = 0\cdot0392$ for 4965 unique reflections with $F > 4\sigma(F)$. The [MoOS$_3$(CuNCS)$_3$]$^{2-}$ anion has an MoS$_3$Cu$_3$ core with atoms at seven vertices of a trigonally distorted cube; the eighth vertex, opposite Mo, is vacant. Mo is tetrahedrally coordinated by one terminal O^{2-} ligand and by three bridging S^{2-} ligands, each of which also bonds to two Cu atoms. Two of the Cu atoms show trigonal-planar coordination by two S^{2-} and one NCS$^-$ ligand bonded *via* N. The third Cu atom has distorted tetrahedral coordination, the fourth ligand atom being S of an NCS$^-$ ligand of a neighbouring anion. Thus anions are linked by pairs of Cu—NCS—Cu bridges to form centrosymmetric dimers. The Mo—O bond length is 1·728 (5) Å; Mo—S range from 2·632 (1) to 2·668 (2) Å, Cu—S from 2·238 (2) to 2·279 (2) Å, Cu—N from 1·866 (5) to 1·893 (5) Å, Mo···Cu from 2·632 (1) to 2·668 (2) Å; Cu—SNC is 2·711 (2) Å. Bonds involving four-coordinate Cu are somewhat longer than those for three-coordinate Cu. The CuNCS linkages are essentially linear at C and only slightly bent at N, but Cu—S—CN for the bridging ligand is 122·0 (2)°.

Experimental. The compound was obtained by reaction of CuSCN with [P(C$_6$H$_5$)$_4$]$_2$[MoOS$_3$] (3:1 molar ratio) in acetone solution and recrystallized from dichloromethane. Crystal size 0·19 × 0·27 × 0·50 mm, Siemens AED2 diffractometer with graphite-mono-chromated Mo $K\alpha$ radiation, cell parameters from 2θ values (20–22°) of 32 reflections measured on both sides of the direct beam. Intensity-data collection in ω/θ scan mode, scan width = 0·51° below α_1 to 0·51° above α_2, scan time = 14–56 s, 2θ_{max} = 45°, h —13→0, k —13→13, l —20→20, no significant variation of three standard reflections, semi-empirical absorption correction, transmission 0·614–0·845, no extinction correction. 6837 reflections measured, all unique, 4965 with $F > 4\sigma(F)$ for structure solution by automatic direct methods and difference syntheses, blocked-cascade refinement on F with $w^{-1} = \sigma^2(F) + 0\cdot00003F^2$, aniso-tropic thermal parameters and constrained phenyl groups [C—C = 1·395, C—H = 0·96 Å, C—C—C =

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* IUPAC name: bis(tetraphenylphosphonium) oxo[1,2,3-tris-(isothiocyanato)-1,2;2,3;3,1-tri-μ-thio-tricuprato(I)-S^1,S^2,S^3]-molybdate(2−).