octamolybdate structures it is evident that the bonding within a cluster is controlled in the first place by the dominant influence of the strong bonds in the *cis* $Mo(O_t)_2$ groups. The weak internal bonds through oxygen bridges are complementary and can vary in length and direction to meet the needs of a particular structure.

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catena-Poly{μ-(2,2'-bipyrimidine-*N,N'* :*N''*,*N'''*)-[(nitrato-*O,O'*)copper(II)]-di-(μ-nitrato-μ-*O*)-[(nitrato-*O,O'*)copper(II)]}, [Cu₂(NO₃)₄(C₈H₆N₄)]

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Abstract. M_r (asymmetric unit) = 266·64, monoclinic, $C2/c$, $a = 19\cdot314$ (3), $b = 7\cdot914$ (1), $c = 15\cdot060$ (2) Å, $\beta = 137\cdot4$ (1)°, $V = 1558$ (3) Å³, $Z = 8$, D_m (by flotation) = 2·26, $D_x = 2\cdot273$ g cm⁻³, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 28\cdot06$ cm⁻¹, $F(000) = 1056$, $T = 293$ K, final conventional $R = 0\cdot039$ for 1248 unique observed reflections. The compound is a polymer built up by complex dimeric units formed by two Cu atoms coordinated by a molecule of the organic ligand and four nitrate groups. Both Cu atoms are six-coordinated with a distorted octahedral geometry, being bonded by two N atoms of the organic ligand, acting as doubly-bidentate, by two O atoms of a bidentate nitrate group and by two O atoms of two monodentate nitrate groups bridging two Cu atoms.

Introduction. Binuclear Cu^{II} complexes with ligands containing N atoms have been widely investigated in recent times since they are of great significance in biological systems (De Munno, Denti & Dapporto, 1983; Thompson, 1983; Dapporto, De Munno, Sega & Mealli, 1984). 2,2'-Bipyrimidine is a ligand with four N donor atoms whose Cu^{II} and Fe^{II} mixed complexes have been synthesized because they are possible models for cytochrome oxidase (Petty, Welch, Wilson, Bottomley & Kadish, 1980; McLendon & Smith, 1982). This ligand is potentially interesting for two reasons: it can act either as a doubly-bidentate bridging ligand or simply as a bidentate ligand. Mononuclear and binuclear 2,2'-bipyrimidine Ru^{II} complexes are known (Dose & Wilson, 1978; Hunziker & Ludi, 1977;

Ruminski & Petersen, 1982). It has also been supposed that this ligand can act as monodentate with $CuCl_2$ in polymeric arrays (Tuerstein, Feit & Navon, 1974). The crystal structure of the title complex has been determined to define the behaviour of the ligand when coordinating to Cu^{II} in the presence of NO_3^- ions.

Experimental. 1 mmol of 2,2'-bipyrimidine in 25 ml of ethanol was added to a solution of 2 mmol of $Cu(NO_3)_2.6H_2O$ in 25 ml of water. A blue crystalline precipitate formed by slow evaporation. Parallelepiped crystal $0.07 \times 0.14 \times 0.14$ mm. Siemens Stoe diffractometer, scan range $2\theta = 3–50°$, graphite-monochromatized Mo $K\alpha$ radiation, $\omega–\theta$ scan technique. 25 reflections with $7° < \theta < 15°$ used for measuring lattice parameters. No systematic loss of intensity of three standard reflections ($1\bar{9}3$, $2,\bar{12},2$, $3\bar{7}3$). 1732 reflections measured with $\theta < 25°$, 1248 unique with $I \geq 3\sigma(I)$, $0 \leq h \leq 18$, $0 \leq k \leq 9$, $\bar{15} \leq l \leq 15$. Absorption ignored. Lp correction. Scattering factors for nonhydrogen atoms (*International Tables for X-ray Crystallography*, 1974, p. 99), and for H atoms (Stewart, Davidson & Simpson, 1965). Anomalousdispersion corrections (*International Tables for X-ray Crystallography*, 1974, p. 149). Structure solved by Patterson and Fourier techniques (Sheldrick, 1976) and refined by a full-matrix least-squares procedure; $\sum w(|F_o| - |F_c|)^2$ minimized; anisotropic thermal parameters for Cu, C, N and O, isotropic for H atoms (from ΔF map); final $R = 0.039$, $R_w = 0.042$, $w = 1/\sigma^2$; max. $\Delta/\sigma = 0.069$, max. and min. $\Delta\rho$ excursions in ΔF synthesis 0.66 and -1.09 e Å^{-3}, respectively. VAX/VMS computer of the Università della Calabria; *SHELX* program (Sheldrick, 1976).

Discussion. Fig. 1 shows a dimeric unit of the complex. Final atomic parameters are reported in Table 1,* bond distances and angles in Table 2. The organic ligand is doubly-bidentate, chelating through its four N atoms; one nitrate group is asymmetrically bidentate [Cu—O(1) 1.952 (4), Cu—O(3) 2.547 (2) Å] and a second is monodentate, asymmetrically bridging two Cu atoms [Cu—O(4) 1.965 (3), Cu—O(4') 2.300 (2) Å]. Every Cu atom is therefore sixcoordinated with a [CuN₂O₄] chromophore. The distortions from octahedral geometry are caused by the organic ligand and by the bidentate nitrate group, which subtend Cu at angles of 82.7 (2) and 55.1 (1)° respectively. On the other hand, the angles N(2)—Cu—O(1) and O(1)—Cu—O(4) are 90.7 (2) and 90.0 (1)° respectively and the atoms N(2), N(1), Cu, O(1), O(4) lie on the same plane. In fact, the deviations

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39661 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
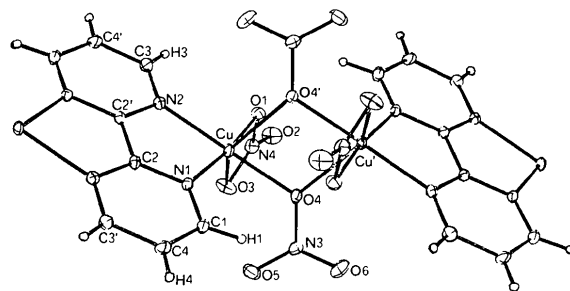

Fig. 1. View of the dimeric unit of the complex.

Table 1. *Fractional atomic coordinates* ($\times 10^5$ *for* Cu; $\times 10^4$ *for* N, C, O; $\times 10^3$ *for* H) *and equivalent isotropic* (*Hamilton*, 1959) *thermal parameters* ($\times 10^3$, *for* Cu $\times 10^4$)

	x	y	z	$U_{eq}(Å^2)$
Cu	−7067 (3)	18149 (4)	43648 (4)	206 (2)
N(1)	226 (2)	3256 (3)	4501 (3)	20 (3)
N(2)	−793 (2)	3920 (3)	5023 (3)	21 (2)
N(3)	−983 (2)	−374 (4)	2608 (3)	31 (2)
N(4)	−2509 (2)	577 (4)	3112 (3)	30 (2)
O(1)	−1618 (2)	636 (3)	4323 (2)	30 (2)
O(2)	−3176 (2)	−266 (4)	2818 (3)	46 (2)
O(3)	−2615 (2)	1379 (4)	2319 (3)	47 (2)
O(4)	−574 (2)	−254 (4)	3778 (2)	28 (2)
O(5)	−1255 (2)	908 (4)	1983 (3)	46 (2)
O(6)	−1061 (4)	−1777 (4)	2233 (4)	81 (5)
C(1)	754 (3)	2905 (5)	4271 (3)	26 (2)
C(2)	277 (2)	4818 (4)	4862 (3)	20 (2)
C(3)	−1292 (3)	4249 (4)	5293 (4)	27 (3)
C(4)	1301 (3)	4154 (4)	4362 (4)	28 (3)
H(1)	78 (3)	179 (5)	411 (4)	25 (10)
H(3)	−159 (3)	363 (5)	528 (4)	22 (10)
H(4)	163 (3)	401 (5)	418 (4)	26 (10)

Table 2. *Bond distances* (Å) *and angles* (°)

Cu—N(1)	2.011 (4)	N(1)—C(1)	1.324 (8)
Cu—N(2)	2.008 (3)	C(1)—H(1)	0.92 (4)
Cu—O(1)	1.952 (4)	C(1)—C(4)	1.378 (7)
Cu—O(3)	2.547 (2)	C(4)—H(4)	0.86 (7)
Cu—O(4)	1.965 (3)	C(4)—C(3')	1.372 (6)
Cu—O(4')	2.300 (2)	N(3)—O(4)	1.301 (5)
C(3)—C(4')	1.372 (6)	N(3)—O(5)	1.209 (4)
C(3)—H(3)	0.75 (6)	N(3)—O(6)	1.204 (5)
C(3)—N(2)	1.317 (9)	N(4)—O(1)	1.293 (3)
N(2)—C(2')	1.331 (5)	N(4)—O(2)	1.210 (6)
C(2')—C(2)	1.432 (8)	N(4)—O(3)	1.230 (6)
C(2)—N(1)	1.325 (4)		
Cu—O(4)—Cu'	106.3 (1)	C(4')—C(3)—N(2)	121.0 (5)
N(2)—Cu—N(1)	82.7 (2)	C(3)—N(2)—C(2')	117.4 (3)
N(2)—Cu—O(1)	90.7 (2)	C(3)—N(2)—Cu	131.4 (3)
O(1)—Cu—O(4)	90.0 (1)	C(2')—N(2)—Cu	111.1 (3)
N(1)—Cu—O(4)	96.6 (2)	N(2)—C(2')—C(2)	117.4 (3)
N(2)—Cu—O(3)	97.9 (1)	C(2')—C(2)—N(1)	117.5 (3)
N(1) Cu—O(3)	126.2 (1)	C(2)—N(1)—Cu	111.1 (4)
O(4)—Cu—O(3)	84.0 (1)	C(2)—N(1)—C(1)	117.7 (4)
O(1)—Cu—O(3)	55.1 (1)	C(1)—N(1)—Cu	131.2 (2)
N(1)—Cu—O(4')	95.7 (1)	N(1)—C(1)—C(4)	120.3 (4)
N(2)—Cu—O(4')	104.5 (1)	C(1)—C(4)—C(3')	118.4 (5)
O(1)—Cu—O(4')	85.4 (1)	O(1)—N(4)—O(2)	119.4 (4)
O(4)—Cu—O(4')	73.7 (1)	O(1)—N(4)—O(3)	116.7 (4)
O(3)—Cu—O(4')	134.7 (1)	O(2)—N(4)—O(3)	123.9 (3)
N(2)—Cu—O(4')	178.1 (1)	O(4)—N(3)—O(5)	118.5 (3)
N(1)—Cu—O(1)	173.4 (1)	O(4)—N(3)—O(6)	116.3 (4)
Cu—O(4)—N(3)	121.3 (2)	O(5)—N(3)—O(6)	125.2 (5)
Cu'—O(4)—N(3)	130.3 (3)		

of these atoms from their mean plane are −0·015 (3), −0·04 (3), 0·0005 (2), −0·021 (2) and −0·008 (2) Å, respectively.

The angle Cu—O(4)—Cu' [106·3 (1)°], which is in agreement with pseudotetrahedral geometry for the O(4) atom, is strictly related to the Cu···Cu' separation of 3·418 (1) Å, which is close to the values found for other dinuclear Cu^{II} complexes (De Munno, Denti & Dapporto, 1983; Dapporto, De Munno, Sega & Mealli, 1984). The bond distances and angles within the 2,2'-bipyrimidine ligand, which is strictly planar [torsion angle N(2)—C(2')—C(2)—N(1) 0·6 (5)°], are in accordance with those previously reported (Fernholt, Rømming & Samdal, 1981), the greatest difference being found in the C(2)—C(2') distance [1·432 (8) Å], which is shorter than the corresponding distance in non-coordinated 2,2'-bipyrimidine [1·511 (2) Å in the gaseous state and 1·497 (4) Å in the solid state], and is also shorter than that found in the coordinated 2,2'-bipyridyl (Procter & Stephens, 1969), which is 1·501 (17) or 1·502 (16) Å in the nitrito-bis(2,2'-bipyridyl)copper(II) nitrate complex. This shortening indicates a greater conjugation which is probably due to the double chelation of the ligand, which with the two Cu^{II} atoms forms a particular conjugate system. The two Cu atoms are in the same plane as the two pyrimidine rings; in fact, the torsion angle C(3)—N(2)—Cu—O(1) is 0·1 (4)° and the dihedral angle between the Cu—N(1)—N(2) and N(1)—N(2)—C(2)—C(2') planes is 176·0 (1)°.

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Structure of Bis(tetraethylammonium) Bis[dimercaptomaleodinitrilato(2−)-*S*,*S'*]-nickelate(II), [N(C$_2$H$_5$)$_4$]$_2$[Ni(C$_4$N$_2$S$_2$)$_2$]

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Abstract. $M_r = 599·57$, triclinic, $P\bar{1}$, $a = 7·5608$ (7), $b = 8·7017$ (9), $c = 12·626$ (3) Å, $\alpha = 93·73$ (1), $\beta = 104·27$ (1), $\gamma = 75·257$ (9)°, $V = 779$ Å^3, $Z = 1$, $D_m = 1·286$, $D_x = 1·279$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 8·54$ cm^{-1}, $F(000) = 318$, $T = 293$ K. Final $R = 0·058$ for 1550 unique observed diffractometer data. The metal atom of the anion has an approximately square-planar configuration and the amino atoms of the cations an approximately tetrahedral configuration. The Ni—S distances are 2·171 (2) and 2·177 (2) Å and the bite angle is 92·3 (1)°. The anion is essentially planar with the Ni atom deviating most by 0·047 (1) Å.

Introduction. The present work forms a part of our research program of structural studies of 1,2-dithiolato complexes of transition metals.

Experimental. Crystals obtained by the procedure of Billig, Williams, Bernal, Waters & Gray (1964). Approximate density measured by flotation in CCl$_4$/benzene showed $Z = 1$.

Unit-cell parameters obtained by least-squares refinement of θ values of 25 high-angle reflections. Crystal 0·1 × 0·3 × 0·25 mm, three-dimensional intensity data collected on an Enraf–Nonius CAD-4 diffractometer