apparently low water content are not known, but it is possible that powders lose some weakly bonded water on exposure to the laboratory atmosphere, although the single crystals did not exhibit loss during the course of the structure determination.

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Structure of *catena*-Poly[tris(pyridine)copper-μ-{*N*-(2-hydroxyiminopropionyl)-L-methioninato(1−)-*O*″,*N*′:*O*}] Nitrate Ethanol Solvate

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Abstract. $[Cu(C_8H_{13}N_2O_4S)(C_5H_5N)_3]NO_3.C_2H_6O$, $M_r = 642.19$, tetragonal, $P4_3$, $a = 9.264\,(3)$, $c = 35.503\,(12)$ Å, $V = 3047$ Å^3, $D_x = 1.398$ g cm^{-3}, $Z = 4$, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5418$ Å, $\mu = 20.8$ cm^{-1}, $F(000) = 1340$, $T = 293$ K, final $R = 0.043$ for 2256 independent reflections. The crystal is built up from complex cations linked into polymeric chains, the outer sphere being occupied by nitrate anions and ethanol solvate molecules. The coordination around Cu is a distorted square bipyramid generated by three pyridine molecules and the oxime-containing anion acting simultaneously in a chelating bidentate mode (*via* the amide O atom and the hydroxyimino N atom) and in a bridging mode (*via* the carboxyl O atom).

Introduction. In continuation of our studies on pyruvoyl amino acid oximes and their metal complexes (Skopenko, Lampeka & Fritsky, 1990), the crystal structure determination of the title complex was carried out. Earlier we reported the preparation and structural study of three ligands of this class: pyruvoylglycine oxime (Lampeka, Dvorkin, Simonov, Fritsky & Skopenko, 1989), pyruvoyl-L-alanine oxime (Dvorkin, Fritsky, Simonov, Lampeka, Mazus & Malinowsky, 1990) and pyruvoyl-L-methionine oxime (H_3Mt) (Dvorkin, Simonov, Skopenko, Fritsky & Lampeka, 1990). It was shown that the mentioned ligands can enter the inner sphere of the metal ions in different ionic forms. A recently performed X-ray investigation of trisodium bis[*N*-(2-hydroxyiminopropionyl)glycinato]cobaltate(III) (Fritsky, Lampeka, Skopenko, Simonov, Dvorkin & Malinowsky, 1993) identified an *N*,*N*,*O*-tridentate chelating mode for the triply charged acido ligand in the complex anion. The present paper reports the structure determination of the mixed ligand complex in which the other possible coordination mode of pyruvoyl amino acid oxime is observed.

Experimental. The complex was synthesized according to the following scheme:

$$Cu(NO_3)_2.3H_2O + H_3Mt + 4py = [Cu(H_2Mt)py_3]NO_3 + (pyH)NO_3 + 3H_2O.$$

A mixture of $Cu(NO_3)_2.3H_2O$ (0.302 g, 1.25 μmol) and pyridine (0.8 ml) in 10 ml of ethanol was added to H_3Mt (0.293 g, 1.25 μmol) dissolved in 5 ml of

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ethanol. Blue-green crystals of the complex were grown from the resulting solution under slow evaporation over $CaCl_2$. The compound is soluble in water and ethanol and virtually insoluble in acetone. The crystals are unstable in air and 2–3 h after removal from the mother liquor lose two pyridine molecules and an ethanol molecule thus being transformed into $[Cu(H_2Mt)py]NO_3$. Therefore the crystal chosen for the X-ray experiment (dimensions $0.2 \times 0.2 \times 0.4$ mm) was coated with shellac film. Unit-cell parameters were calculated from the setting angles of 12 reflections ($18 \leq 2\theta \leq 28°$) on a RED-4 diffractometer using the least-squares technique. Systematic absences ($00l$, $l \neq 4n$) suggest two possible space groups: $P4_1$ and $P4_3$, corresponding to the different (right and left, respectively) crystal enantiomers. Intensity data were collected on a DAR-UMB diffractometer, ω–$\theta/2\theta$ scan, $(\sin\theta)/\lambda < 0.597$ Å^{-1}, $h = -7$ to 8, $k = 0$ to 11, $l = 0$ to 36, 2576 independent reflections, 2256 with $I > 3\sigma(I)$, ΔI in standard reflections $< 3\%$. Lorentz–polarization correction, no absorption correction. The Cu position was obtained from a Patterson map, the other non-H atoms from a Fourier synthesis. H-atoms from differential Fourier synthesis except those of the ethanol molecule because of their considerable thermal vibrations in the crystal. The nitrate anion is found to be disordered between two positions with approximately equal occupancy. The structure was refined anisotropically for non-H and isotropically for H atoms, taking anomalous dispersion on non-H atoms into account, 452 parameters refined, F magnitudes and unit weights, $(\Delta/\sigma)_{max} = 0.70$ for non-H atoms and 0.95 for H atoms, $\Delta\rho_{max} = 0.35$ and $\Delta\rho_{min} = -0.43$ e Å^{-3}. Refinement was carried out independently for the two space groups $P4_1$ ($R = 0.045$) and $P4_3$ ($R = 0.043$). Hamilton's (1965) test made it possible to give preference with 99.5% probability to the $P4_3$ group, corresponding to the left configuration of the α-C atom. The *SHELX76* program (Sheldrick, 1976) and an SM-4 computer were used for the calculations. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^4$) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
Cu	−454 (1)	6148 (1)	−193	300
S	3913 (4)	1234 (3)	−644 (1)	899
O(1)	7181 (5)	6114 (5)	−236 (1)	409
O(2)	6501 (5)	7174 (6)	−769 (2)	459
O(3)	2029 (5)	6158 (6)	−236 (2)	447
O(4)	−923 (5)	7974 (5)	−909 (2)	428
N(1)	3740 (5)	6318 (6)	−684 (2)	349
N(2)	66 (5)	7232 (5)	−691 (2)	300
C(1)	5184 (17)	599 (13)	−318 (5)	1436
C(2)	3722 (9)	3090 (9)	−501 (3)	591
C(3)	5043 (8)	3996 (8)	−572 (3)	461
C(4)	4848 (7)	5583 (8)	−457 (2)	335
C(5)	6292 (6)	6384 (7)	−493 (2)	351
C(6)	2402 (6)	6564 (7)	−556 (2)	306
C(7)	1384 (7)	7336 (7)	−808 (2)	300
C(8)	1847 (8)	8150 (9)	−1144 (2)	484
N(3)	−472 (6)	8108 (6)	84 (2)	399
C(9)	757 (11)	8707 (10)	217 (3)	626
C(10)	786 (14)	9970 (12)	416 (4)	842
C(11)	−522 (14)	10657 (11)	500 (3)	742
C(12)	−1762 (15)	10069 (12)	364 (4)	809
C(13)	−1721 (10)	8792 (10)	166 (3)	622
N(4)	−449 (6)	5164 (6)	324 (2)	358
C(14)	765 (8)	4995 (9)	527 (2)	459
C(15)	830 (10)	4538 (11)	883 (3)	609
C(16)	−456 (9)	4162 (9)	1061 (2)	500
C(17)	−1723 (9)	4270 (9)	856 (2)	471
C(18)	−1687 (8)	4759 (8)	492 (2)	427
N(5)	−470 (6)	4217 (5)	−488 (2)	377
C(19)	39 (9)	2967 (8)	−344 (2)	544
C(20)	−93 (14)	1697 (10)	−536 (3)	781
C(21)	−696 (11)	1624 (9)	−876 (3)	675
C(22)	−1219 (10)	2859 (10)	−1021 (3)	623
C(23)	−1085 (8)	4134 (8)	−825 (2)	466
N(6)*	−2977 (23)	4515 (25)	−1889 (4)	1729
O(5)*	−1903 (23)	3710 (25)	−1962 (4)	1929
O(6)*	−3514 (23)	5309 (25)	−2136 (4)	3065
O(7)*	−3466 (23)	4491 (25)	−1566 (4)	1033
N(6)*	−2966 (14)	4310 (15)	−1911 (4)	638
O(5)*	−2202 (14)	3238 (15)	−2007 (4)	1524
O(6)*	−4209 (14)	4468 (15)	−2042 (4)	937
O(7)*	−2450 (14)	5238 (15)	−1680 (4)	1817
O(8)	−6231 (10)	5365 (11)	−1494 (3)	1276
C(24)	−7271 (10)	4381 (11)	−1505 (3)	2122
C(25)	−7977 (10)	4572 (11)	−1892 (3)	1892

* Denotes atoms of the disordered nitrate anion.

Discussion. Positional and thermal parameters are given in Table 1,* bond distances and angles in Table 2 and selected torsion angles in Table 3. A *PLUTO* (Motherwell & Clegg, 1978) drawing of the complex unit is shown in Fig. 1.

The structure consists of the $[Cu(H_2Mt)py_3]^+$ complex cation units linked by the bridging carboxyl groups into polymeric chains in the **a** direction and the outer sphere molecules (NO_3^- and C_2H_5OH) are associated with them. The Cu···Cu separation in the neighbouring cations is equal to parameter a (Fig. 2). Space group $P4_3$ determines the packing of the chains as being away from each other at 1/4 period along the c axis according to the tetragonal rule. The empty spaces in the crystal are filled by the disordered NO_3^- groups and ethanol molecules.

The coordination polyhedron of Cu^{II} is an axially distorted square bipyramid formed by the N atoms of three pyridine molecules arranged in a meridional fashion (Cu—N = 2.047–2.073 Å) and by the donor atoms of the monoanion H_2Mt^-. In the latter the hydroxyimino N and amide O atoms chelate the Cu

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55827 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1013]

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

Copper coordination polyhedron

Cu—O(1)^{i}	2.196 (4)	Cu—N(3)	2.065 (6)
Cu—O(3)	2.305 (4)	Cu—N(4)	2.049 (6)
Cu—N(2)	2.090 (6)	Cu—N(5)	2.073 (5)

O(1)^{i}—Cu—O(3)	172.1 (2)	O(3)—Cu—N(5)	88.7 (2)
O(1)^{i}—Cu—N(2)	100.2 (2)	N(2)—Cu—N(3)	89.0 (2)
O(1)^{i}—Cu—N(3)	92.2 (2)	N(2)—Cu—N(4)	166.2 (2)
O(1)^{i}—Cu—N(4)	93.4 (2)	N(2)—Cu—N(5)	89.0 (2)
O(1)^{i}—Cu—N(5)	86.8 (2)	N(3)—Cu—N(4)	88.0 (2)
O(3)—Cu—N(2)	73.2 (2)	N(3)—Cu—N(5)	177.9 (2)
O(3)—Cu—N(3)	92.1 (2)		

Pyruvoyl-L-methionine oxime anion

O(1)—C(5)	1.253 (8)	N(2)—C(7)	1.294 (8)
O(2)—C(5)	1.240 (9)	C(1)—S	1.752 (17)
O(3)—C(6)	1.244 (8)	C(2)—S	1.801 (9)
O(4)—N(2)	1.384 (7)	C(2)—C(3)	1.506 (11)
O(4)—H(O4)	0.81 (8)	C(3)—C(4)	1.537 (10)
N(1)—C(4)	1.473 (9)	C(4)—C(5)	1.535 (9)
N(1)—C(6)	1.341 (8)	C(6)—C(7)	1.486 (9)
N(1)—H(N1)	1.08 (1)	C(7)—C(8)	1.474 (11)

C(1)—S—C(2)	101.6 (6)	C(3)—C(4)—C(5)	109.7 (5)
N(1)—O(4)—H(O4)	108 (6)	O(1)—C(5)—O(2)	126.2 (6)
C(4)—N(1)—C(6)	122.3 (6)	O(1)—C(5)—C(4)	114.5 (6)
C(4)—N(1)—H(N1)	119 (6)	O(2)—C(5)—C(4)	119.2 (6)
C(6)—N(1)—H(N1)	119 (6)	O(3)—C(6)—N(1)	121.1 (6)
C(6)—C(7)—C(8)	123.4 (6)	O(3)—C(6)—C(7)	121.3 (5)
O(4)—N(2)—C(7)	114.0 (5)	N(1)—C(6)—C(7)	117.5 (6)
S—C(2)—C(3)	113.9 (6)	N(2)—C(7)—C(6)	111.6 (6)
C(2)—C(3)—C(4)	113.1 (6)	N(2)—C(7)—C(8)	125.0 (6)
N(1)—C(4)—C(3)	112.2 (6)	N(1)—C(4)—C(5)	109.7 (6)

Pyridine rings

N(3)—C(9)	1.351 (12)	C(15)—C(16)	1.393 (13)
N(3)—C(13)	1.350 (11)	C(16)—C(17)	1.385 (12)
C(9)—C(10)	1.368 (15)	C(17)—C(18)	1.371 (12)
C(10)—C(11)	1.400 (18)	N(5)—C(19)	1.351 (9)
C(11)—C(12)	1.361 (18)	N(5)—C(23)	1.328 (10)
C(12)—C(13)	1.376 (15)	C(19)—C(20)	1.367 (13)
N(4)—C(14)	1.344 (9)	C(20)—C(21)	1.331 (16)
N(4)—C(18)	1.346 (9)	C(21)—C(22)	1.345 (13)
C(14)—C(15)	1.337 (13)	C(22)—C(23)	1.378 (12)

C(9)—N(3)—C(13)	117.0 (7)	C(15)—Cl(6)—C(17)	117.9 (7)
N(3)—C(9)—C(10)	123.2 (9)	C(16)—Cl(7)—C(18)	120.0 (8)
C(9)—C(10)—C(11)	118.8 (11)	C(17)—Cl(8)—N(4)	122.1 (7)
C(10)—C(11)—C(12)	118.3 (10)	C(19)—N(5)—C(23)	116.2 (6)
C(11)—C(12)—C(13)	120.1 (11)	C(5)—C(19)—C(20)	121.1 (8)
C(12)—C(13)—N(3)	122.4 (9)	C(19)—C(20)—C(21)	122.4 (9)
C(14)—N(4)—C(18)	116.3 (5)	C(20)—C(21)—C(22)	117.0 (9)
N(4)—Cl(4)—C(15)	125.6 (7)	C(21)—C(22)—C(23)	120.2 (9)
C(14)—Cl(5)—C(16)	118.0 (8)	C(22)—C(23)—N(5)	123.0 (7)

Symmetry code: (i) $-1+x, y, z$.

ion [Cu—N(oxime) = 2.090 Å; Cu—O(amide) = 2.306 Å], the carboxyl O atom being bridging (Cu—O = 2.196 Å). The axial Cu—O distances differ from each other by 0.11 Å, the differences in the basal Cu—N distances do not exceed 0.04 Å. The angular parameters at the Cu atom are in the range of 86.8–100.2°, chelate angle N2—Cu—O3 is decreased to 73.2°. The Cu coordination sphere is additionally stabilized by the pseudochelate Cu—O(1)′—C(5)′—O(2)′···H(O4)—O(4)—N(2) formed *via* the hydrogen bond O(4)—H(O4)···O(2)′ = 2.547 Å [O(4)—H(O4) = 0.81, O2′···H(O4) = 1.74 Å; angle O(4)—H(O4)—O(2)′ = 174.5°].

Table 3. *Selected torsion angles* (°) *in coordinated and free pyruvoyl*-L-*methionine oxime*

	H_2Mt^-	H_3Mt
O(4)—N(2)—C(7)—C(6)	177.9 (16)	178.4
N(2)—C(7)—C(6)—N(1)	165.8 (13)	−0.8
C(8)—C(7)—C(6)—N(1)	−15.8 (17)	−179.1
C(7)—C(6)—N(1)—C(4)	179.1 (17)	−176.2
C(6)—N(1)—C(4)—C(5)	−135.9 (16)	−129.9
N(1)—C(4)—C(5)—O(1)	160.7 (11)	−172.8

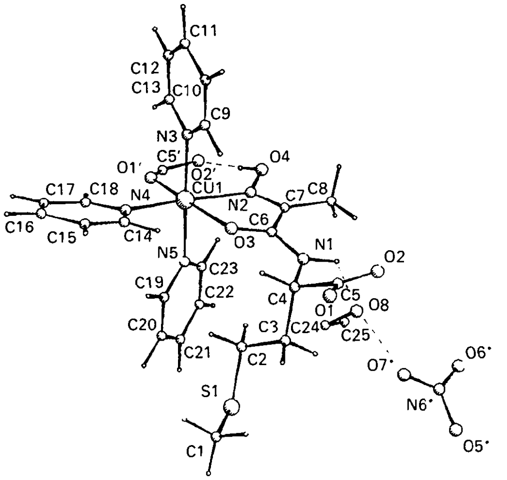

Fig. 1. View of the complex cation unit with outer sphere molecules showing the numbering scheme. Two symmetry-related O atoms and one C atom are included to complete the coordination sphere. One of the disordered nitrate anions is omitted for clarity.

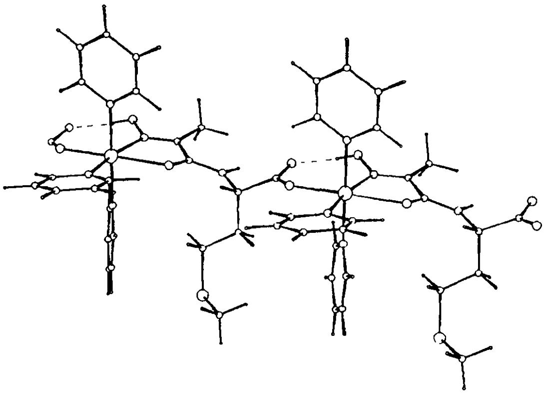

Fig. 2. Fragment of the structure displaying the linkage of two translational complex cations into the polymeric chain.

The geometrical parameters of the coordinated H_2Mt^- are close to those seen in the free H_3Mt quoted above. The coordination causes some changes in the conformation of the backbone and the thioether side chain as compared to H_3Mt (Table 3). The chelate formation forces the hydroxyimino group to turn from a *trans* to a *cis* position with reference to the amide carbonyl group. Unlike the free ligand, the hydroxyimino group in the complex is in a *cis* position with reference to the amide carbonyl, which is dictated by the chelate formation. The dihedral angle between the carboxyl group and the nearly planar anion framework is $\simeq 22°$, whereas in the free H_3Mt it is $\simeq 47°$.

In the coordinated pyridine rings the average distances are N—C = 1.345 and C—C = 1.368 Å; the bond angles near N are $\simeq 116.5°$ and near C are $\simeq 120.7°$. The dihedral angles between pyridine molecules and the chelate ring are: A,B = 101.7; A,C = 122.1; A,M = 93.5; B,C = 94.8; B,M = 14.6; C,M = 89.1° (A, B, C = pyridine molecules; M = chelate).

The ethanol molecule is linked to the complex cation by the hydrogen bond N1—H(N1)···O(8) = 3.01 Å [H(N1)—O(8) = 2.25, N1—H(N1) = 1.08 Å; N1—H(N1)···O(8) = 126°]. The nitrate ions have normal N—O distances (1.23–1.28 Å) and bond angles (117.8–121.3°). The short contacts O(8)···O(7) = 2.70 Å and O(8)···O(6)* = 2.83 Å can be interpreted as hydrogen bonds.

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Structures of Triphenylantimony(V) Dibromide and Dichloride

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Abstract. (1) Dibromotriphenylantimony(V), $[SbBr_2(C_6H_5)_3]$, $M_r = 513.0$, orthorhombic, $Fdd2$, $a = 24.179$ (8), $b = 10.282$ (3), $c = 14.234$ (5) Å, $V = 3538.7$ Å^3, $Z = 8$, $D_x = 1.93$ g cm^{-3}, Mo $K\alpha$ radiation (graphite monochromator), $\lambda = 0.7107$ Å, $\mu = 63.6$ cm^{-1}, $F(000) = 1952$, $T = 294$ K, $R = 0.0428$, $wR = 0.0451$, for 96 least-squares parameters and 739 unique observed reflections with $I > 3\sigma(I)$. The Sb atom and one of the phenyl groups lie on a twofold axis. (2) Dichlorotriphenylantimony(V), $[SbCl_2(C_6H_5)_3]$, $M_r = 423.9$, orthorhombic, $P2_12_12_1$, $a = 10.882$ (4), $b = 12.127$ (4), $c = 12.986$ (4) Å, $V = 1713.7$ Å^3, $Z = 4$, $D_x = 1.64$ g cm^{-3}, Mo $K\alpha$ radiation (graphite monochromator), $\lambda = 0.7107$ Å, $\mu = 19.3$ cm^{-1}, $F(000) = 832$, $T = 294$ K, $R = 0.0272$, $wR = 0.0274$, for 190 least-squares parameters and 1555 unique observed reflections with $I > 3\sigma(I)$. In both compounds, the Sb atom is in trigonal bipyramidal coordination with two axial halogen atoms [Sb—Br 2.632 (1); Sb—Cl 2.468 (2), 2.458 (2) Å] and three equatorial phenyl groups [Sb—C 2.11 (1) and 2.12 (1) Å for the bromide and 2.084 (2), 2.100 (2) and 2.106 (2) Å for the chloride].

Introduction. There is current interest in the structures of Group 15 compounds with the stoichiometry Ph_3MX_2 (X = halogen) as, contrary to most expectations, both triphenylphosphorus diiodide (Godfrey, Kelley, McAuliffe, Mackie, Pritchard & Watson, 1991) and triphenylarsenic diiodide (McAuliffe, Beagley, Gott, Mackie, MacRory & Pritchard, 1987; Beagley, Colburn, El-Sayrafi, Gott, Kelley, Mackie, McAuliffe, MacRory & Pritchard, 1988) have an unusual four-coordinate structure in which the iodine–iodine bond remains intact. This contrasts with the five-coordinate trigonal bipyramidal arrangement with axial halogen atoms and equatorial phenyl groups about the Group 15 atom in Ph_3AsF_2 (Augustine, Ferguson & March, 1975), Ph_3SbCl_2 (Polynova & Porai-Koshits, 1966) and Ph_3BiCl_2 (Hawley & Ferguson, 1968). The triphenylantimony dichloride structure was solved from film data, and refined to a final R value of 0.17. The structure of triphenylantimony dichloride as a weak

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