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Acta Cryst. (1983). C**39**, 1214–1216

Structure of [1,3-Dimethyl-2,4,5,6(1*H*, 3*H*)-pyrimidinetetrone 5-oximato][1,3-dimethyl-2,4,5,6(1*H*, 3*H*)-pyrimidinetetrone 5-oxime]silver(I), $[Ag(C_6H_6N_3O_4)(C_6H_7N_3O_4)]$

By C. Ruiz-Valero, A. Monge, E. Gutiérrez-Puebla and E. Gutiérrez-Ríos

Instituto de Química Inorgánica Elhuyar, Serrano 113, *Madrid*-6, *Spain and Departamento de Química Inorgánica, Facultad de Químicas, Universidad Complutense, Madrid*-3, *Spain*

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Abstract. $M_r = 477 \cdot 14$, orthorhombic, $P2_12_12_1$, $a = 6 \cdot 345$ (5), $b = 14 \cdot 01$ (2), $c = 17 \cdot 92$ (2) Å, $V = 1593$ (3) Å^3, $Z = 4$, $D_x = 1 \cdot 99$ Mg m^{-3}, μ(Mo $K\alpha$) = $1 \cdot 31$ mm^{-1}, λ(Mo $K\alpha$) = $0 \cdot 71069$ Å, $F(000) = 952$, $T = 291$ K, $R = 0 \cdot 06$ for 1667 observed reflexions. The Ag atom is coordinated with two organic bidentate ligands, of the same asymmetric unit, and with one O atom of a neighbouring molecule, forming a chain structure. No Ag—Ag interaction occurs.

Introduction. This investigation has been undertaken because of the increasing interest in the coordination of the Ag^+ ion with organic bidentate ligands. In this work we report the crystal structure of the title compound, prepared by J. D. López-González and co-workers, at the Department of Inorganic Chemistry of the University of Granada (Spain).

Experimental. Fibrous red needle-like crystal, $0 \cdot 5 \times 0 \cdot 2 \times 0 \cdot 2$ mm. Nonius CAD-4F automatic diffractometer. Cell dimensions refined by least-squares fitting of the θ values of 25 reflexions. 3336 unique reflexions, $1° < \theta < 33°$, h,k,l range from 0,0,0 to 9,21,26, monochromatic Mo $K\alpha$ radiation, $\omega/2\theta$ scans. Due to radiation damage a progressive decrease in intensities occurred. To account for this effect, three standard reflexions were monitored periodically and the time limit for a final scan was 45 s. Intensities scaled from the variations of the three standard reflexions whose intensities fell to 50% at the end of the data collection. Intensities corrected for Lorentz and polarization effects, 1667 considered observed [$I > 2\sigma(I)$]. No absorption corrections ($\mu R = 0 \cdot 65$). Scattering factors for neutral atoms and anomalous-dispersions corrections for Ag from *International Tables for X-ray Crystallography* (1974). Structure solved by three-dimensional Patterson and Fourier syntheses allowing the location of all non-hydrogen atoms. Anisotropic full-matrix least-squares refinement using F's and unit weights led to $R = 0 \cdot 69$ with 244 parameters refined. H atoms of the methyl groups fixed at calculated positions. The oxime H(21) was located on a difference synthesis calculated with reflexions having $\sin \theta/\lambda < 0 \cdot 5$ Å^{-1} as the highest peak of the map. In order to prevent bias on ΔF *vs* F_o or $\sin \theta/\lambda$, the last steps of the refinement were carried out with weights $w = 1/(a + b|F_o|)^2$ where $a = 4 \cdot 33$, $b = 0 \cdot 15$ if $|F_o| < 20$ and $a = 0 \cdot 76$, $b = 0 \cdot 03$ if $|F_o| > 20$, calculated by *PESOS* (Martinez-Ripoll & Cano, 1975). Final refinement with fixed isotropic temperature factors and coordinates for H atoms gave $R = 0 \cdot 060$, and $R_w = 0 \cdot 067$.* Maximum and average shift/error: $0 \cdot 3386$ and $0 \cdot 0610$ respectively. A final difference synthesis had no electron density $>0 \cdot 56$ e Å^{-3}, and $<-0 \cdot 40$ e Å^{-3}. Most of the calculations were carried out with XRAY70 (Stewart, Kundell & Baldwin, 1970).

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* Lists of structure amplitudes, anisotropic thermal parameters and H atom parameters (six half-atoms per methyl group) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38588 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. Table 1 shows the final atomic parameters. Fig. 1 (Johnson, 1965) shows the geometry of the structure and the atom labelling. Table 2 lists the bond lengths and angles.

The Ag atom is coordinated with two organic bidentate ligands, of the same asymmetric unit, and with one O atom of a nearest-neighbour molecule, forming a chain structure. No Ag—Ag interaction occurs, as the shortest Ag—Ag distance is 3·75 (1) Å.

Since the distance Ag—O($14^{\rm ii}$)* is 3·007 (12) Å, O($14^{\rm ii}$) of a symmetry-related anionic ligand is weakly bonded to Ag. This distance may be compared with the sum of the covalent radii of Ag and O, 2·18 Å (Pauling, 1960), and the sum of the van der Waals radii, 3·20 Å (Bondi, 1964).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ag	0·63704 (17)	0·27732 (7)	0·94822 (7)	425 (4)
C(11)	0·5999 (17)	0·0514 (8)	0·9606 (7)	262 (35)
C(12)	0·6415 (23)	−0·0487 (8)	0·9724 (7)	305 (34)
C(13)	0·3296 (20)	−0·0918 (9)	0·9020 (7)	323 (39)
C(14)	0·4000 (21)	0·0777 (9)	0·9206 (8)	339 (40)
C(15)	0·5648 (22)	−0·2159 (8)	0·9515 (10)	474 (42)
C(16)	0·0947 (22)	0·0281 (12)	0·8489 (9)	491 (54)
C(21)	0·9164 (18)	0·4517 (9)	0·8627 (7)	268 (35)
C(22)	1·0042 (22)	0·5462 (10)	0·8472 (8)	370 (44)
C(23)	1·2808 (24)	0·4594 (10)	0·7763 (8)	363 (42)
C(24)	1·0022 (24)	0·3618 (10)	0·8341 (8)	387 (43)
C(25)	1·3082 (25)	0·6311 (10)	0·7918 (9)	452 (51)
C(26)	1·2730 (24)	0·2882 (11)	0·7565 (11)	620 (61)
O(11)	0·8701 (20)	0·1094 (6)	1·0232 (7)	595 (39)
O(12)	0·8015 (17)	−0·0773 (6)	1·0058 (6)	515 (38)
O(13)	0·2206 (17)	−0·1517 (7)	0·8728 (7)	518 (38)
O(14)	0·3468 (18)	0·1619 (7)	0·9094 (7)	509 (36)
O(21)	0·6502 (15)	0·5170 (7)	0·9279 (5)	439 (32)
O(22)	0·9336 (19)	0·6211 (7)	0·8635 (7)	612 (43)
O(23)	1·4421 (16)	0·4616 (9)	0·7400 (7)	602 (42)
O(24)	0·9325 (17)	0·2829 (8)	0·8456 (7)	567 (37)
N(11)	0·7025 (17)	0·1247 (7)	0·9837 (7)	320 (32)
N(12)	0·5154 (19)	−0·1158 (7)	0·9407 (7)	372 (35)
N(13)	0·2829 (16)	0·0046 (8)	0·8943 (6)	289 (32)
N(21)	0·7405 (17)	0·4380 (9)	0·9015 (6)	353 (35)
N(22)	1·1986 (16)	0·5412 (8)	0·8073 (6)	292 (31)
N(23)	1·1902 (19)	0·3721 (7)	0·7915 (6)	358 (37)

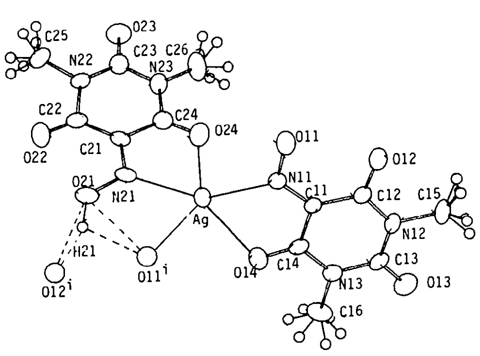

Fig. 1. An *ORTEP* (Johnson, 1965) perspective drawing of title compound showing the numbering scheme.

O(21) of the acid ligand is linked to the anionic ligand of the nearest-neighbour molecule through an asymmetrically bifurcated hydrogen bond, of the type reported by Monge, Martínez-Ripoll & García-Blanco (1978). The geometrical features of the hydrogen-bond network are shown in Fig. 2.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

E.s.d.'s are *ca* 0·011 Å and 0·6° for lengths and angles involving Ag, and 0·017 Å and 1° for other non-hydrogen atoms.

Ag—O(14)	2·548	C(16)—N(13)	1·481
Ag—O(24)	2·627	C(21)—C(22)	1·463
Ag—O($11^{\rm i}$)	2·378	C(21)—C(24)	1·465
Ag—N(11)	2·270	C(21)—N(21)	1·328
Ag—N(21)	2·490	C(22)—O(22)	1·178
C(11)—C(12)	1·442	C(22)—N(22)	1·428
C(11)—C(14)	1·503	C(23)—O(23)	1·213
C(11)—N(11)	1·284	C(23)—N(22)	1·376
C(12)—O(12)	1·245	C(23)—N(23)	1·378
C(12)—N(12)	1·359	C(24)—O(24)	1·208
C(13)—O(13)	1·207	C(24)—N(23)	1·424
C(13)—N(12)	1·410	C(25)—N(22)	1·465
C(13)—N(13)	1·390	C(26)—N(23)	1·432
C(14)—O(14)	1·243	O(11)—N(11)	1·295
C(14)—N(13)	1·350	O(21)—N(21)	1·333
C(15)—N(12)	1·449	O(21)—H(21)	0·99

N(11)—Ag—N(21)	153·8	N(22)—C(23)—N(23)	120
N(11)—Ag—O($11^{\rm i}$)	134·3	O(23)—C(23)—N(23)	119
N(21)—Ag—O($11^{\rm i}$)	69·9	O(23)—C(23)—N(22)	121
O(24)—Ag—N(21)	63·2	C(21)—C(24)—N(23)	114
O(24)—Ag—N(11)	95·4	C(21)—C(24)—O(24)	126
O(24)—Ag—O($11^{\rm i}$)	129·7	O(24)—C(24)—N(23)	119
O(14)—Ag—N(21)	132·3	N(21)—O(21)—H(21)	128
O(14)—Ag—N(11)	67·1	Ag—O(14)—C(14)	111
O(14)—Ag—O(24)	110·1	Ag—O(24)—C(24)	114
O(14)—Ag—O($11^{\rm i}$)	88·1	C(11)—N(11)—O(11)	117
C(14)—C(11)—N(11)	113	Ag—N(11)—O(11)	117
C(12)—C(11)—N(11)	130	Ag—N(11)—C(11)	125
C(12)—C(11)—C(14)	118	C(13)—N(12)—C(15)	119
C(11)—C(12)—N(12)	120	C(12)—N(12)—C(15)	119
C(11)—C(12)—O(12)	122	C(12)—N(12)—C(13)	122
O(12)—C(12)—N(12)	117	C(14)—N(13)—C(16)	118
N(12)—C(13)—N(13)	117	C(13)—N(13)—C(16)	116
O(13)—C(13)—N(13)	121	C(13)—N(13)—C(14)	126
O(13)—C(13)—N(12)	122	C(21)—N(21)—O(21)	115
C(11)—C(14)—N(13)	117	Ag—N(21)—O(21)	121
C(11)—C(14)—O(14)	123	Ag—N(21)—C(21)	122
O(14)—C(14)—N(13)	121	C(23)—N(22)—C(25)	117
C(24)—C(21)—N(21)	112	C(22)—N(22)—C(25)	118
C(22)—C(21)—N(21)	123	C(22)—N(22)—C(23)	125
C(22)—C(21)—C(24)	125	C(24)—N(23)—C(26)	117
C(21)—C(22)—N(22)	112	C(23)—N(23)—C(26)	119
C(21)—C(22)—O(22)	128	C(23)—N(23)—C(24)	123
O(22)—C(22)—N(22)	120		

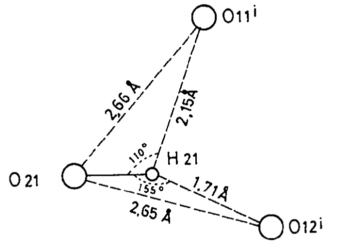

Fig. 2. Schematic drawing showing the geometrical features of the hydrogen-bond network. E.s.d.'s are 0·01 and 0·15 Å for O···O and O···H distances and 12° for the angles at H.

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* Symmetry code: (i) $x-\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}+2$; (ii) $x+\frac{1}{2}, \bar{y}+\frac{1}{2}, \bar{z}+2$.

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Redetermination of the Structure of (Isothiocyanato)(2,2′,2′′-triaminotriethylamine)-nickel(II), [$Ni(C_6H_{18}N_4)(NCS)_2$]

By B. D. Santarsiero* and V. Schomaker

Department of Chemistry, University of Washington, Seattle, Washington 98125, *USA*

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Abstract. $M_r = 321·11$, $P2_12_12_1$, $a = 10·852$ (1), $b = 8·6460$ (6), $c = 14·724$ (2) Å, $V = 1381·5$ (2) Å^3, $Z = 4$, $D_x = 1·544$ (1) g cm^{-3}, Nb-filtered Mo *Kα* radiation ($\lambda = 0·71069$ Å), $F(000) = 672$, $\mu = 16·8$ cm^{-1}, $T \approx 290$ K, $R = 0·060$, $S = 1·21$, 3235 reflections, 172 parameters. Quasi-octahedral coordination around Ni with average Ni—N(tren) and Ni—NCS bond lengths 2·12 and 2·09 Å. All bond lengths normal, including the N—C bond lengths of the tertiary N atom of tren, in contrast to earlier reports [Cradwick & Hall (1970). *Acta Cryst.* B**26**, 1384–1385, and references therein]. Both NCS groups essentially linear, 178 [1]°, but slightly bent at N, Ni—N—C 161 [3]°; average N—C and C—S bond lengths 1·153 [3] and 1·638 [1] Å.

Introduction. On comparing our recent structural results on Co^{III}–tren complexes with the reports on other tren complexes, we noticed that the most recent results for Ni(tren)(NCS)$_2$ [Cradwick & Hall (1970), C&H hereafter] were obviously still inaccurate and also, by present standards, rather imprecise.

Experimental. Dark blue 0·3 × 0·5 × 0·3 mm crystal from a hot aqueous stoichiometric solution of $NiCl_2$, tren, and KSCN, upon standing. Space group $P2_12_12_1$ (confirming the previous reports) by oscillation and Weissenberg photographs (*h*00 absent for *h* odd, 0*k*0 absent for *k* odd, 00*l* absent for *l* odd). Diffractometry: Picker FACS-1, Nb-filtered Mo *Kα* radiation, crystal mounted roughly along **b**. Lattice constants by least-squares refinement of average 2θ values from four settings on a Syntex $P2_1$ diffractometer (Mo *Kα*, graphite monochromator), '$\pm 2\theta$' hkl and '$\pm 2\theta$' $\bar{h}\bar{k}\bar{l}$, 15 reflections. Intensity measurements: 3530 reflections $hk\pm l$, $2\theta \leq 55°$, by 1° min^{-1} θ–2θ scans of 2θ width 1·2° plus the α_1–α_2 angular dispersion; 20-s post-scan stationary-counter–stationary-crystal background counts fore and aft. Six check reflections, every 150 reflections – no decomposition and $g = 0·006$, used in $\sigma_I^2 = S + r^2B + (gI)^2$, for scan count S, total background count B, scan-to-total-background time ratio $r = t_s/t_b$, and net intensity $I = S - rB$. Reduction: $F_o = \sqrt{I/\mathrm{Lp}}$, $w_{F_o} = 4(\mathrm{Lp}F_o/\sigma_I)^2$, no absorption corrections applied (ratio of extreme absorption factors, A_{min}/A_{max}, roughly 0·8). Form factors from *International Tables for X-ray Crystallography* (1962), and for H from *International Tables* (1974), including f' and f'' for Ni and S.

Initial non-H coordinates from C&H with $U = 0·032$ Å^2 estimated by *NORMSF* (the XRAY76 system, Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), and H-atom coordinates by *BONDAT* (the XRAY76 system) for idealized bond angles, 0·99 Å C—H and N—H bond lengths, and $U = 0·050$ Å^2. Least-squares minimization of $\sum w(F_o - |F_c|)^2$ on all parameters but H-atom coordinates, 172 parameters and 3235 reflections in the final cycle, 204 F's with both F_o and $|F_c|$ less than $2\sigma_{F_o}$ and 44 with $|\Delta F|/\sigma_{F_o} > 3·9$ rejected, the 44 still included in R and R_w. Final R 0·060, R_w 0·046, and S 1·21 (enantiomer: R 0·069, R_w 0·054 and S 1·38); max. and average

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[*] Present address: Arthur Amos Noyes Laboratory of Chemical Physics, 127-72, California Institute of Technology, Pasadena, CA 91125, USA.

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