Preparation and Crystal Structure of the Complexes Thallium(I) Oxalohydroxamate(1−) and Malonohydroxamate(1−)†

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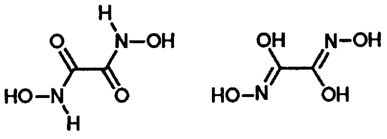
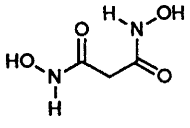
Thallium(I) oxalohydroxamate **1**, Tl(HONHCOCONHO), and malonohydroxamate **2**, Tl(HONHCO-CH_2CONHO), have been characterized as acid salts of type A_2 and B_2, respectively, using single-crystal X-ray diffraction. In **1** the co-ordination polyhedron around the Tl^I can be described as a distorted dodecahedron; the eight Tl–O bonds are divided into sets of six short and two long, the latter lying at one side of the Tl^I the lone-pair electrons of which are stereoactive. In **2** the co-ordination environment of Tl^I is square pyramidal with the lone-pair electrons oriented in the axial direction.

As a coolant ingredient of propellants, oxalohydroxamic acid has been extensively studied by physical and chemical methods. Its crystal structure was determined independently by Lowe-Ma and Decker[1] and Begum *et al.*[2] and the crystal structure of its ammonium salt, which can be used as a monopropellant, was also reported.[3,4] These studies revealed that in both cases the oxalohydroxamate moiety exists primarily in the oxamic rather than the oximic form, and strong intermolecular hydrogen bonding is formed in the crystalline state. On the other hand, hydroxamic acids are the classical colorimetric and gravimetric reagents for many metals,[5] and their ability to chelate metal centres has been proposed to be responsible for their inhibitory effect on several metal-containing enzymes.[6–8] General interest in their biochemical activity has led to a series of theoretical and experimental studies on the structures of hydroxamic acids[9–11] and their metal complexes.[12,13] In the present work, the thallium(I) salts of two dihydroxamic acids, namely oxalohydroxamic acid and malonohydroxamic acid, were investigated in regard to their mode of metal–ligand bonding and the stereoactivity of the lone-pair electrons of the metal atom.



oxamic form oximic form

oxalohydroxamic acid



malonohydroxamic acid

Experimental

Both crystalline compounds were prepared by dissolving $TlCO_3$ in an aqueous solution of the acid in a 1:4 molar ratio, followed by slow evaporation of the resulting solution at room temperature.

Crystallography.—Crystal data for Tl(HONHCOCONHO) **1**. $C_2H_3N_2O_4Tl$, $M = 323.40$, monoclinic, space group $C2/c$ (no. 15), $a = 12.961(2)$, $b = 4.0478(5)$, $c = 9.883(2)$ Å, $\beta = 97.52(1)°$, $U = 514.0(2)$ Å^3, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 4.179$ g cm^{-3}. Colourless plates with (100) well developed. Crystal dimensions 0.20 × 0.22 × 0.28 mm, μ(Mo-Kα) = 316.7 cm^{-1}.

Crystal data for Tl(HONHCOCH_2CONHO) **2**. $C_3H_5N_2O_4Tl$, $M = 337.45$, monoclinic, space group Pn (alternative setting of Pc, no. 7) $a = 4.5263(8)$, $b = 7.744(2)$, $c = 9.388(2)$ Å, $\beta = 102.72(1)°$, $U = 321.0(1)$ Å^3, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 3.491$ g cm^{-3}. Colourless plates. Crystal dimensions 0.08 × 0.20 × 0.25 mm, μ(Mo-Kα) = 253.67 cm^{-1}.

Data collection and processing. Nicolet R3m/V diffractometer, ω–2θ mode with ω scan width = 0.65° below Kα_1 to 0.65° above Kα_2, ω scan speed 1.50–15.00° min^{-1}, graphite-monochromated Mo-Kα radiation. Intensity data collected at room temperature were processed with the profile-fitting procedure of Diamond[14] and corrected for absorption using ψ-scan data[15] (maximum, minimum transmission factors = 0.022, 0.001 for **1** and 0.017, 0.002 for **2**, respectively). For compound **1** 734 reflections measured ($3 \leqslant 2\theta \leqslant 55°$, $hk \pm l$), 597 unique (merging R = 0.071), giving 552 with $I > 5\sigma(I)$. Two standard reflections [(112), (312)] monitored after every 125 data measurements showed only random fluctuations of ±2%. For compound **2** 2001 reflections measured ($3 \leqslant 2\theta \leqslant 75°$, $hk \pm l$), 1832 unique (merging R = 0.047), giving 1091 with $I > 10\sigma(I)$. Two standard reflections [$(10\bar{1})$, $(10\bar{3})$] monitored after every 125 data measurements showed only random fluctuations of ±2%.

Structure analysis and refinement. Both structures **1** and **2** were solved by the Patterson method and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the methylene and amine groups were generated geometrically (C–H and N–H bonds fixed at 0.96 Å); the hydroxy protons were located from reasonable peaks in the Fourier difference maps. All H atoms were assigned appropriate isotropic thermal parameters and included in structure-factor calculations. The weighting scheme used was $w = 1/[\sigma^2(F_o) + g|F_o|^2]$ with $g = 0.0020$ for **1** and 0.0025 for **2**. For compound **2** the Rogers η parameter[16] refined to 0.92(12) so that the reported atomic coordinates correspond to the correct absolute structure.[17] Final R and R' values are 0.064 and 0.083 for **1**, and 0.073 and 0.097 for **2**. Computations were performed on a DEC MicroVAX-II computer with the SHELXTL-PLUS program package.[18] Analytical expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[19]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

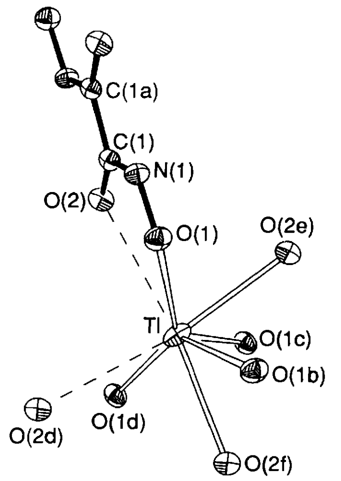

Fig. 1 Perspective view of the interaction between the thallium(I) atom and its neighbouring ligands in complex **1**. Symmetry codes are given in Table 3

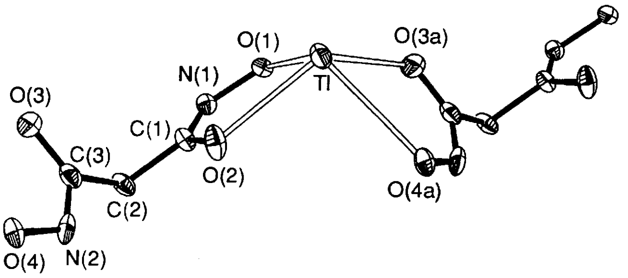

Fig. 2 Perspective view of the co-ordination environment of the thallium(I) atom in complex **2** with the atom numbering scheme

Table 1 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Tl	0	790(2)	2500
C(1)	2021(9)	6550(36)	4707(14)
N(1)	1595(10)	4923(38)	5664(13)
O(1)	730(9)	3039(29)	5344(12)
O(2)	1689(8)	6520(33)	3468(11)

Table 2 Atomic coordinates (× 10^5 for Tl, × 10^3 for other atoms) for complex **2**

Atom	*x*	*y*	*z*
Tl	0	83 822(8)	0
O(1)	403(3)	753(2)	231(2)
O(2)	359(4)	560(2)	−16(2)
O(3)	321(4)	127(3)	109(2)
O(4)	334(3)	38(2)	−171(2)
N(1)	545(3)	595(2)	227(2)
N(2)	524(3)	168(2)	−88(2)
C(1)	517(4)	510(2)	106(2)
C(2)	708(3)	343(2)	115(2)
C(3)	494(4)	202(2)	38(2)

The final atomic positional parameters for compounds **1** and **2** are listed in Tables 1 and 2, and bond distances and angles related to the thallium co-ordination geometry are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 3 Co-ordination geometry (bond lengths in Å, angles in °) of the thallium(I) atom in complexes **1** and **2**

Tl(HONHCOCONHO) **1**			
Tl–O(1)	2.99(1)	Tl–O(1b)	2.89(1)
Tl–O(2)	3.25(1)	Tl–O(2e)	2.85(1)
O(1)–Tl–O(1b)	64.2(4)	O(1)–Tl–O(1c)	139.7(4)
O(1b)–Tl–O(1c)	115.2(5)	O(1)–Tl–O(1d)	144.5(5)
O(1)–Tl–O(2)	52.2(4)	O(1b)–Tl–O(2)	116.0(4)
O(1c)–Tl–O(2)	109.1(4)	O(1d)–Tl–O(2)	100.2(4)
O(1)–Tl–O(2e)	74.6(3)	O(1b)–Tl–O(2e)	74.9(3)
O(1c)–Tl–O(2e)	67.2(3)	O(1d)–Tl–O(2e)	129.4(3)
O(2)–Tl–O(2e)	82.9(3)	O(2)–Tl–O(2f)	171.7(3)
O(2e)–Tl–O(2f)	105.5(5)	O(2)–Tl–O(2d)	88.8(4)
Tl(HONHCOCH$_2$CONHO) **2**			
Tl–O(1)	2.59(1)	Tl–O(3a)	2.74(2)
Tl–O(2)	2.72(2)	Tl–O(4a)	2.88(2)
O(1)–Tl–O(2)	61.7(5)	O(1)–Tl–O(4a)	104.1(4)
O(1)–Tl–O(3a)	71.3(5)	O(2)–Tl–O(4a)	90.2(5)
O(2)–Tl–O(3a)	113.1(5)	O(3a)–Tl–O(4a)	57.9(5)

Symmetry transformations: a $(x, 1 + y, z)$; b $(-x, -y, 1 - z)$; c $(x, -y, -\frac{1}{2} + z)$; d $(-x, y, \frac{1}{2} - z)$; e $(x, -1 + y, z)$; f $(-x, -1 + y, \frac{1}{2} - z)$.

Discussion

As illustrated in Fig. 1, the co-ordination polyhedron around the thallium(I) atom in complex **1** can be described as a distorted dodecahedron, with the four symmetrically related O(1) atoms constituting the elongated tetrahedron and the other set of four related O(2) atoms composing the compressed tetrahedron. The eight Tl–O bonds are divided into six short (primary, < 3.0 Å, shown by open lines in Fig. 1) and two long (secondary, > 3.2 Å, shown by broken lines in Fig. 1) bonds such that the latter two are *cis* to each other, indicating that the lone-pair electrons of thallium(I) are stereoactive in this complex.

The oxalohydroxamate group occupies a centrosymmetric site and acts as a planar, doubly chelating ligand. Its molecular dimensions are essentially identical to those found in free oxalohydroxamic acid,[1,2] and the C=O bond length of 1.24(2) Å and C–N bond length of 1.33(2) Å indicate that the oxalohydroxamate ligand exists in the oxamic form. The hydrogen atom H(O1) on a crystallographic two-fold axis gives rise to a symmetric strong O–H–O hydrogen bond of 2.50(1) Å so that this complex is an acid salt of type A_2 according to Speakman's definition.[20] The oxalohydroxamate groups comprise a hydrogen-bonded, two-dimensional ligand layer whose mean plane matches the (400) plane; layers of this type are, in turn, interlinked by the aforementioned strong hydrogen bonds to form a three-dimensional network, which is consolidated by covalent bonding to the Tl^I atoms located at the interstices between the ligand layers.

In complex **2** the co-ordination environment of the Tl^I atom is square pyramidal with the metal lone-pair electrons pointing in the axial direction (Fig. 2). The Tl^I atom is displaced by 1.57(2) Å above the basal plane composed of the four oxygen atoms. The four Tl–O bonds are strong (< 2.90 Å) and other contacts between Tl and O atoms are all longer than 3.45 Å. The relatively long C=O bonds [1.27(2) and 1.27(3) Å] and short C–N bonds [1.29(3) and 1.25(3) Å] suggest the existence of keto–enol tautomerism for the organic ligand in this crystal. The hydrogen atom, H(4), of the hydroxyl group as found on a difference map is at 0.97(1) Å from O(4) and 1.58(1) Å from O(1) with an O(4)–H(4)···O(1b) angle of 176(1)°, and this asymmetrical strong hydrogen bond characterizes complex **2** as an acid salt of type B_2.[20] In this complex, each malonohydroxamate ligand acts as a bridge between two thallium centres to generate a one-dimensional polymer, and these polymers are further interlinked by hydrogen bonds to form a three-dimensional crystal structure.

The ground-state electronic configuration of thallium(I) is $6s^2$. Although such a pair of s electrons beyond a completed shell is always stereoactive in the thallium(I) complexes with lower co-ordination number (three to five), this activity cannot be predicted in complexes with higher co-ordination number (six to twelve). Brown and Faggiani[21] have investigated the factors affecting the co-ordination of Tl^I and pointed out that it will form short bonds, have a low co-ordination number and a stereoactive lone pair when the counter ion is a strong base (strength >0.22 valence unit), but otherwise will form longer bonds with a co-ordination number of six or more. According to the expressions and parameters suggested by Brown and co-workers,[21,22] the Lewis-base strengths of the oxalohydroxamate anion in **1** and the malonohydroxamate anion in **2** were calculated as 0.187 and 0.267 valence unit, respectively. According to the theory of Brown and Faggiani,[21] these two ligands are moderate and strong Lewis bases, respectively, and Tl^I is expected to be high- and low-co-ordinated with a stereoactive lone pair of electrons in the oxalohydroxamate and malonohydroxamate complexes. The present experimental results are basically consistent with the prediction of Brown and Faggiani.

Appendix

Calculation of Base Strength.—The Lewis base strengths of the oxalohydroxamate and malonohydroxamate ions were calculated using the second method suggested by Brown and Faggiani.[21] The residual valence on each independent O atom is obtained by subtracting the valence of the internal bonds from the atomic valence of O (=2.0) and dividing by the number of external bonds each O atom must form to give it a co-ordination number of four. The mean value for all independent O atoms is the base strength of the ligand.

The bond valences for O–H and O–C bonds were calculated through equation (A1) where s is the bond valence, R the

$$s = (R/R_1)^{-N} \qquad \text{(A1)}$$

observed bond length, R_1 the bond length expected for a bond of unit valence and N an empirical constant. For an O–H bond, $R_1 = 0.87$, $N = 2.2$;[22] for an O–C bond, $R_1 = 1.436$, $N = 2.926$.[21]

For an O–N bond, the expression $s \approx (R/R_1{}^{-(0.6\nu+2.2)}$ was used,[22] where ν is a typical co-ordination number for the atom bound to the O atom; in this case, $\nu = 3$ and $R_1 = 1.396$[23] were used.

Complex **1**

O(1)

O(1)–N(1)	1.36 Å	$s = 1.110$
O(1)–H(O1)	1.25 Å	$s = 0.451$

$$s_{O(1)} = (2 - 1.110 - 0.451)/(4 - 2) = 0.220$$

O(2)

O(2)–C(1)	1.24 Å	$s = 1.536$
O(2)$\cdots$H(N1)	2.01 Å	$s = 0.158$

$$s_{O(2)} = (2 - 1.536 - 0.158)/(4 - 2) = 0.153$$
$$s_{\text{ligand}} = (0.220 + 0.153)/2 = 0.187$$

Complex **2**

O(1)

O(1)–N(1)	1.39 Å	$s = 1.017$
O(1)$\cdots$H(4)	1.58 Å	$s = 0.269$
O(1)$\cdots$H(2)	1.86 Å	$s = 0.188$

$$s_{O(1)} = 2 - 1.017 - 0.269 - 0.188 = 0.526$$

O(2)

O(2)–C(1)	1.27 Å	$s = 1.433$
O(2)$\cdots$H(1)	1.84 Å	$s = 0.192$

$$s_{O(2)} = (2 - 1.433 - 0.192)/(4 - 2) = 0.188$$

O(3)

O(3)–C(3)	1.27 Å	$s = 1.433$

$$s_{O(3)} = (2 - 1.43)/(4 - 1) = 0.189$$

O(4)

O(4)–N(2)	1.44 Å	$s = 0.883$
O(4)–H(4)	0.97 Å	$s = 0.787$

$$s_{O(4)} = (2 - 0.883 - 0.787)/(4 - 2) = 0.165$$
$$s_{\text{ligand}} = (0.526 + 0.188 + 0.189 + 0.165)/4 = 0.267$$

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References

1 C. K. Lowe-Ma and D. L. Decker, *Acta Crystallogr., Sect. C*, 1986, **42**, 1648.
2 A. S. Begum, V. K. Jain, C. L. Khetrapal and N. C. Shivaprakash, *J. Crystallogr. Spectrosc. Res.*, 1987, **17**, 545.
3 A. S. Begum and V. K. Jain, *Acta Crystallogr., Sect. C*, 1988, **44**, 1047.
4 R. E. Marsh, *Acta Crystallogr., Sect. C*, 1989, **45**, 347.
5 R. C. Mehrotra, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, p. 505.
6 N. E. Dixon, J. A. Hinds, A. K. Fihelly, C. Gazzola, D. J. Winzor, R. L. Blakeley and B. Zerner, *Can. J. Biochem.*, 1980, **58**, 1323.
7 S. H. Wilkes and J. M. Prescott, *J. Biol. Chem.*, 1983, **258**, 13517.
8 J. O. Baker, S. H. Wilkes, M. E. Bayliss and J. M. Prescott, *Biochemistry*, 1983, **22**, 2098.
9 E. Lipczynska-Kochany and H. Iwamura, *J. Org. Chem.*, 1982, **47**, 5277.
10 R. Hilal and H. Moustafa, *Int. J. Quantum Chem.*, 1984, **26**, 183.
11 I. K. Larsen, *Acta Crystallogr., Sect. B*, 1988, **44**, 527.
12 H. J. Lindner and S. Göttlicher, *Acta Crystallogr., Sect. B*, 1969, **25**, 832.
13 P. G. Harrison, T. J. King and R. C. Phillips, *J. Chem. Soc., Dalton Trans.*, 1976, 2317.
14 R. Diamond, *Acta Crystallogr., Sect. A*, 1969, **25**, 43.
15 G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A*, 1968, **24**, 348.
16 D. Rogers, *Acta Crystallogr., Sect. A*, 1981, **37**, 734.
17 P. G. Jones, *Acta Crystallogr., Sect. A*, 1987, **43**, 79.
18 G. M. Sheldrick, in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, New York, 1985, p. 175.
19 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 55, 99, 149 (now distributed by Kluwer Academic Publishers, Dordrecht).
20 J. C. Speakman, *Struct. Bonding (Berlin)*, 1972, **12**, 141.
21 I. D. Brown and R. Faggiani, *Acta Crystallogr., Sect. B*, 1980, **36**, 1802.
22 I. D. Brown and K. K. Wu, *Acta Crystallogr., Sect. B*, 1976, **32**, 1957.
23 F. H. Allen, O. Kennard, D. G. Waston, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

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