The structures of some Cu^{II} complexes of linear aliphatic tetraamines have been reported. A comparison of the selected structural data of these complexes with those of the title compound is given in Table 4. These structural data are expected to influence the kinetic properties of these complexes. This aspect is being taken up shortly.

Table 4. *Selected structural data for* Cu^{II}– *tetraamine complexes*

Linear aliphatic tetraamines of the type $H_2N(CH_3)_lNH(CH_2)_m$-$NH(CH_2)_nNH_2$ are denoted by the symbol *l,m,n*-tet.

	Cu(2,2,2-tet)(SCN)$_2$	Cu(2,3,2-tet)(ClO$_4$)$_2$	Cu(3,2,3-tet)(ClO$_4$)$_2$	Cu(3,3,3-tet)(ClO$_4$)$_2$
Cu—N (Å) distance	2·008 (7)– 2·030 (5)	2·016 (6)– 2·032 (6)	2·012 (8)– 2·031 (8)	2·02 (2)– 2·04 (2)
Cu—O (Å) distance	–*	2·667 (5) 2·527 (5)	2·539 (7)	
Chelate angle for 5-membered ring (°)	84·6 (3) 84·3 (2) 84·7 (3)	85·3 (2) 85·3 (3)	85·1 (3)	
Chelate angle for 6-membered ring (°)		93·9 (2)	90·1 (4) 93·3 (4)	92·7 (7) 97·7 (7) 85·3 (7)
trans N—Cu—N (°)	154·0 161·0	176·4 (3) 178·5 (4)	173·3 (4) 176·2 (3)	159·4 (7) 169·4 (7)
Coordination geometry about Cu^{II}	distorted square pyramidal	tetragonally distorted octahedral	square pyramidal	tetragonally distorted octahedral
Conformation of chelate rings	*gauche*, *gauche*, *gauche*	*gauche*, chair, *gauche*	chair *gauche* chair	chair, chair, chair
References	Marongiu, Lingafelter & Paoletti (1969)	Fawcett Rudich, Toby, Lalancette, Potenza & Schugar (1980)	Present work	Fawcett Rudich, Toby, Lalancette, Potenza & Schugar (1980)

* The Cu—S bond distance for this complex is 2·607 (2) Å.

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The Chain Polymeric Structure of Lead(II) Crotonate

BY WILLIAM CLEGG, IAN R. LITTLE AND BRIAN P. STRAUGHAN

*Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE*1 7*RU, England*

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Abstract. *catena*-μ_3-(Crotonato-μ-*O*,μ-*O*′)-(crotonato-*O*,*O*′)-lead(II), $[Pb(C_4H_5O_2)_2]$, $M_r = 377·4$, triclinic, $P\bar{1}$, $a = 5·1930$ (4), $b = 7·3386$ (6), $c = 13·1528$ (12) Å, $\alpha = 98·797$ (8), $\beta = 91·668$ (8), $\gamma = 94·059$ (8)°, $V = 493·70$ Å^3, $Z = 2$ monomeric units, $D_x = 2·538$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 17·2$ mm^{-1}, $F(000) = 344$, $T = 295$ K, $R = 0·036$ for 1621 observed reflections. Pb is coordinated by two chelating crotonate ligands, one of which is additionally bonded *via* both O atoms to further Pb atoms to produce a polymeric chain. The Pb coordination geometry is distorted pentagonal pyramidal, with the site opposite the apex occupied by a stereochemically active lone pair of electrons. Pb—O bond lengths are in

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the range 2·350 (6)–2·635 (7) Å; the shortest Pb···O is 3·426 (9) Å.

Introduction. The structure of lead(II) crotonate was determined as part of a study of metal complexes of simple α,β-unsaturated carboxylates. The unusual structure of zinc(II) crotonate consists of binuclear triply-bridged units, Zn$_2$(crotonate)$_3^+$, linked by the remaining crotonate to form chains (Clegg, Little & Straughan, 1986*a*). The present work was carried out in the light of similarities between the vibrational spectra of lead(II) and zinc(II) crotonates, and the variety of coordination numbers and geometries commonly adopted by lead(II) carboxylates (Rajaram & Rao, 1982; Dzhafarov, Amiraslanov, Nadzhafov, Movsumov & Mamedov, 1981; Houttemane, Boivin, Thomas, Canonne & Nowogrocki, 1981; Beveridge & Bushnell, 1979; Cingi, Manfredotti, Guastini & Musatti, 1975).

Experimental. Compound prepared from lead(II) carbonate and crotonic acid in refluxing water; crystals obtained from the solution by cooling overnight. Crystal mounted on glass fibre, 0·31 × 0·21 × 0·08 mm, Siemens AED2 diffractometer, cell parameters from 2θ values of 32 reflections measured at $\pm\omega(20 < 2\theta < 25°)$, 1868 reflection intensities measured with $2\theta < 50°$, h −6→0, k −8→8, l −15→15, corrections for minor intensity variations of three standard reflections, semi-empirical absorption corrections based on ellipsoid model and sets of equivalent reflections measured at a range of azimuthal angles, transmission 0·019–0·058. 1733 unique reflections ($R_{\rm int} = 0{\cdot}019$), 1621 with $F > 4\sigma(F)$ used in analysis. Structure solved from Patterson and difference syntheses, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0{\cdot}00055F^2$, H atoms constrained to give C—H = 0·96 Å on external C—C=C angles or in rigid methyl groups with H—C—H = 109·5°, $U(\mathrm{H}) = 1{\cdot}2U_{\rm eq}(\mathrm{C})$, anisotropic thermal parameters for non-H atoms, extinction $x = 4{\cdot}2\,(6)\times10^{-6}$ [$F_c' = F_c/(1 + xF_c^2/\sin2\theta)^{1/4}$], scattering factors from *International Tables for X-ray Crystallography* (1974). 125 parameters, $R = 0{\cdot}036$, $wR = 0{\cdot}045$, slope of normal probability plot = 1·44, max. $\Delta/\sigma = 0{\cdot}022$, mean = 0·001, $(\Delta\rho)_{\max} = 1{\cdot}61$, $(\Delta\rho)_{\min} = -1{\cdot}69$ e Å^{-3}, with major features close to Pb. Programs: *SHELXTL* (Sheldrick, 1985).

Discussion. Atomic coordinates are given in Table 1,* bond lengths and angles in Table 2. The polymeric structure is shown in Fig. 1. Each Pb atom is coordinated by two chelating crotonate ligands, one more asymmetric than the other. Each oxygen atom of the more symmetrically bonded crotonate [O(21) and O(22)] is also coordinated to another Pb atom, to form the polymeric chain. Thus Pb is six-coordinate, the geometry being that of a distorted pentagonal pyramid. The basal coordinating atoms are those involved in bridging to other Pb atoms in the chain, together with one of the O atoms of the crotonate group which is bonded exclusively and asymmetrically to this Pb atom: the other O atom of this group forms the apex of the pentagonal pyramid, and this Pb—O bond is the shortest [2·350 (6) Å]. The basal Pb—O bond lengths are all in the range 2·512 (6)–2·635 (7) Å. Distortions from a regular pentagonal pyramidal geometry are necessary in order to accommodate the narrow 'bite' of the bidentate crotonate ligands. In particular, O(12) lies 1·52 (1) Å above the mean plane of the other basal oxygen atoms, for which r.m.s. Δ = 0·00 (1) Å.

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

$U_{\rm eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	$U_{\rm eq}$
Pb	1808 (1)	2713 (1)	546 (1)	378 (1)
O(11)	−1958 (11)	2829 (9)	1495 (5)	482 (21)
O(12)	1544 (12)	3060 (12)	2502 (5)	635 (27)
C(11)	−829 (15)	2982 (12)	2387 (7)	410 (26)
C(12)	−2547 (16)	2945 (13)	3280 (7)	452 (28)
C(13)	−1619 (18)	2857 (15)	4208 (8)	531 (31)
C(14)	−3227 (24)	2768 (21)	5130 (10)	758 (49)
O(21)	−1603 (13)	3673 (8)	−757 (5)	482 (21)
O(22)	−1450 (13)	763 (8)	−681 (6)	501 (22)
C(21)	−2499 (15)	2021 (12)	−1032 (6)	401 (26)
C(22)	−4735 (21)	1551 (13)	−1745 (8)	511 (31)
C(23)	−5902 (17)	2746 (13)	−2212 (7)	464 (28)
C(24)	−8187 (18)	2296 (16)	−2948 (8)	548 (33)

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

Pb—O(11)	2·350 (6)	Pb—O(12)	2·554 (7)
Pb—O(21)	2·635 (7)	Pb—O(22)	2·512 (6)
Pb—O(21*a*)	2·634 (6)	Pb—O(22*b*)	2·578 (6)
O(11)—C(11)	1·281 (11)	O(12)—C(11)	1·233 (10)
C(11)—C(12)	1·498 (13)	C(12)—C(13)	1·311 (14)
C(13)—C(14)	1·500 (17)	O(21)—C(21)	1·262 (10)
O(22)—C(21)	1·245 (11)	C(21)—C(22)	1·459 (13)
C(22)—C(23)	1·316 (15)	C(23)—C(24)	1·495 (13)

O(11)—Pb—O(12)	53·1 (2)	O(11)—Pb—O(21)	77·4 (2)
O(12)—Pb—O(21)	126·8 (2)	O(11)—Pb—O(22)	77·8 (2)
O(12)—Pb—O(22)	123·3 (2)	O(21)—Pb—O(22)	49·5 (2)
O(11)—Pb—O(21*a*)	83·9 (2)	O(12)—Pb—O(21*a*)	86·7 (3)
O(21)—Pb—O(21*a*)	68·1 (2)	O(22)—Pb—O(21*a*)	117·3 (2)
O(11)—Pb—O(22*b*)	85·1 (2)	O(12)—Pb—O(22*b*)	82·8 (3)
O(21)—Pb—O(22*b*)	114·1 (2)	O(22)—Pb—O(22*b*)	64·7 (3)
O(21*a*)—Pb—O(22*b*)	168·0 (2)	Pb—O(11)—C(11)	96·6 (5)
Pb—O(12)—C(11)	88·3 (6)	O(11)—C(11)—O(12)	122·0 (8)
O(11)—C(11)—C(12)	116·5 (7)	O(12)—C(11)—C(12)	121·5 (8)
C(11)—C(12)—C(13)	121·8 (8)	C(12)—C(13)—C(14)	124·6 (9)
Pb—O(21)—C(21)	92·4 (5)	Pb—O(21)—Pb(*a*)	112·0 (2)
C(21)—O(21)—Pb(*a*)	153·9 (6)	Pb—O(22)—C(21)	98·8 (5)
Pb—O(22)—Pb(*b*)	115·3 (3)	C(21)—O(22)—Pb(*b*)	144·9 (5)
O(21)—C(21)—O(22)	119·0 (7)	O(21)—C(21)—C(22)	121·8 (8)
O(22)—C(21)—C(22)	119·2 (8)	C(21)—C(22)—C(23)	124·6 (8)
C(22)—C(23)—C(24)	125·6 (9)		

Symmetry operators: (*a*) −*x*, 1 − *y*, −*z*; (*b*): −*x*, −*y*, −*z*.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43036 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The closest Pb···O contact is 3·426 (9) Å, to O(11*c*) in the next polymeric chain [O(11) displaced one unit cell along *a*; symmetry operation $x + 1, y, z$ is denoted by the added *c*]. This Pb···O vector is inclined at over 50° to the vacant coordination site opposite the vertex of the pentagonal pyramid [O(11*c*)···Pb—O(11) = 127·1 (2)°]. The O atoms most nearly in line with the vacant axial position are O(21*c*) and O(22*c*), 3·94 (1) and 4·15 (1) Å respectively from Pb [O(21*c*)···Pb—O(11) = 167·3 (2), O(22*c*)···Pb—O(11) = 159·3 (2)°]. These are too remote to be considered as bonded to Pb to give any form of distorted pentagonal bipyramidal or capped pyramidal coordination. Rather, the vacant coordination site is occupied by a stereochemically active lone pair of electrons, which, according to Nyholm–Gillespie VSEPR theory, exhibits a larger repulsive effect than does a pair of bonding electrons. This effect is manifested in the observed distortion of the basal atoms of the pyramid away from the lone pair and towards the apex: *all* O(11)—Pb—O(basal) angles are <90°. Thus, all six coordinating O atoms lie within one hemisphere around the Pb atom, which lies 0·262 (1) Å below the mean basal plane defined by O(21), O(22), O(21*a*) and O(22*b*).

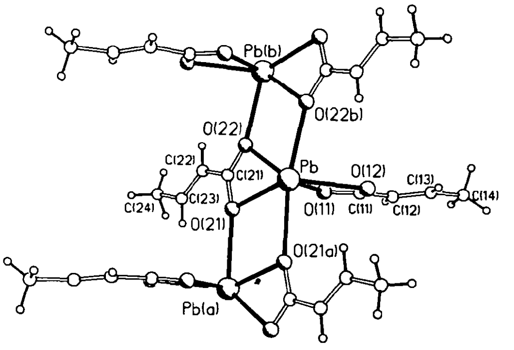

Fig. 1. Part of the polymeric chain, showing the atom labelling.

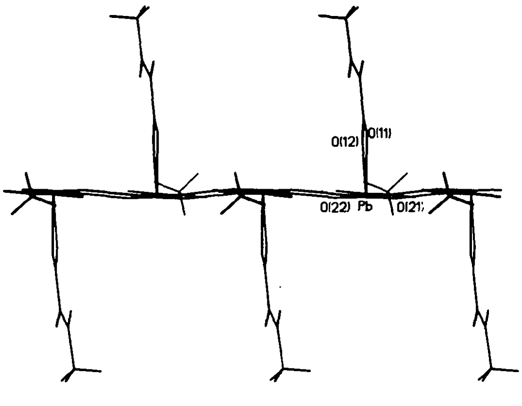

Fig. 2. Side view of the polymeric chain.

The geometry of the crotonate ligands is not unusual. The greater asymmetry of coordination by the crotonate occupying the apical [O(11)] and one basal position [O(12)] is reflected in its C—O bond lengths, which differ more than those of the second crotonate. The asymmetrical C—O lengths of 1·28 (1) and 1·23 (1) Å are similar to those (1·31 and 1·22 Å) in the monodentate bridging ligands of Zn_3(crotonate)$_6$(quinoline)$_2$, which contains four bidentate and two monodentate crotonate bridges (Clegg, Little & Straughan, 1985). The C and O atoms of each crotonate ligand are essentially coplanar [r.m.s. $\Delta = 0{\cdot}04$ (1) and 0·02 (1) Å], as in other complexes of crotonate with Zn and Cu (Clegg, Little & Straughan, 1985, 1986*a*,*b*; Bukowska-Strzyzewska, Skoweranda, Heyduk & Mrozinski, 1983).

Both PbOCO chelate rings are virtually planar [r.m.s. $\Delta = 0{\cdot}006$ (5) and 0·020 (5) Å]. The Pb_2O_2-rhombs of the polymeric chain are exactly planar, lying on inversion centres. Thus the chain is composed of alternate planar Pb_2O_2 and PbO_2C four-membered rings sharing Pb—O edges, the interplanar angles all being under 10°. This arrangement is very similar to the chain polymeric structure of bis(*p*-aminobenzoato)lead(II) (Amiraslanov, Dzhafarov, Nadzhafov, Mamedov, Movsumov & Usubaliev, 1980): in this structure, the Pb_2O_2 rings deviate somewhat from planarity, but the PbOCO chelate rings are essentially planar [the non-planarity of one ring described in this publication is incorrect, being based on wrongly tabulated Pb—O—Pb angles]. The major difference between the two structures is in the Pb coordination. The relative orientation of the two chelating ligands is quite different, so that the six-coordinate Pb atom in the *p*-aminobenzoate complex is described as having a distorted trigonal prismatic geometry.

The near-coplanarity of the edge-linked four-membered rings making up the polymeric chain in lead(II) crotonate, and the essential planarity of the crotonate ligands, means that, within each chain, all the Pb atoms and the C and O atoms of the bridging crotonate ligands lie close to a single plane; the non-bridging ligands protrude alternately above and below this plane (Fig. 2).

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Structure of Bis(1-thia-4,7-diazacyclononane)cobalt(III) Perchlorate

BY TREVOR W. HAMBLEY

Department of Inorganic Chemistry, University of Sydney, Sydney 2006, *Australia*

AND LAWRENCE R. GAHAN

Department of Chemistry, University of Queensland, St Lucia, Queensland 4067, *Australia*

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Abstract. $[Co(C_6H_{14}N_2S)_2](ClO_4)_3$, M_r = 649·8, orthorhombic, *Pmnn*, a = 8·838 (2), b = 10·652 (2), c = 12·606 (2) Å, V = 1186·8 Å^3, Z = 2, D_x = 1·818 g cm^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 12·35 cm^{-1}, $F(000)$ = 668, T = 294 K, final R = 0·055 for 945 reflections. The tridentate macrocyclic ligands coordinate in an arrangement having *trans* S atoms with Co—S 2·238 (1) Å and Co—N 1·984 (3) Å. The geometry about Co is approximately octahedral. The C atoms of the nine-membered ring show disorder.

Introduction. The stereochemistries, electron-transfer and spectral properties of thioether complexes, particularly those of multidentate ligands, have been the subject of recent and extensive studies. The complex $[Co(daes)_2]Cl_3.2H_2O$ [daes = di(aminoethyl) sulfide] has been structurally characterized (Hammershoi, Larsen & Larsen, 1978) and adopts a geometry with the S atoms in *cis* positions. All attempts to prepare an isomer with *trans* S atoms proved unsuccessful (Searle & Larsen, 1976). Preparation and spectral analysis of the complex $[Co(tasn)_2]^{3+}$ (tasn = 1-thia-4,7-diazacyclononane) gave equivocal results; the absorption spectrum was similar to that of $[Co(daes)_2]^{3+}$, suggesting that the *cis* isomer was again the one formed, while the ^{13}C NMR spectrum indicated the presence of more than one isomer (Gahan, Lawrence & Sargeson, 1982). However, chromatographic techniques which are normally successful at separating such isomers failed to achieve any separation in this case.

In order to establish the geometry adopted by the title complex we have determined its structure and report it here.

Experimental. Complex prepared as described previously (Gahan *et al.*, 1982); crystals obtained by ethanol vapour diffusion into a water solution of the perchlorate salt. Data collected using Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation, space group *Pmnn*;* 25 independent reflections with 19° ≤ 2θ ≤ 25° used for least-squares determination of cell constants; intensities of three standard reflections monitored, less than 1% decomposition. Structure solved by heavy-atom method with *SHELX*76 (Sheldrick, 1976); H atoms included at calculated sites (C—H and N—H, 0·97 Å). Co, N, S and Cl atoms anisotropic, all others isotropic. Full-matrix least-squares refinement based on F values converged with shifts $< 0.05\sigma$ in positional parameters of non-H atoms. Maximum excursions in a final difference map, ±0·7 e Å^{-3}. All calculations performed with *SHELX*76 (Sheldrick, 1976). Scattering factors (neutral Co for Co^{III}) and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974). Data-collection and refinement parameters are given in Table 1. Final positional parameters are listed in Table

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* Non-standard setting of *Pnnm*. Equivalent positions: $\pm(x, y, z;\ x, -y, -z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z;\ \tfrac{1}{2}+x, \tfrac{1}{2}+y, \tfrac{1}{2}-z)$.

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