thiocarbamate]platinum(II) (Bardi, Del Pra, Piazzesi & Berto, 1981), 2·303 (5) Å in chlorotris[*O*-ethyl (*N*-propyl)thiocarbamate]platinum(II) chloride (Bardi, Piazzesi, Del Pra, Celeste, Faraglia & Trincia, 1985), 2·296 (6) Å in dichloro[*O*-methyl(*N*-allyl)thiocarbamate]palladium(II) (Porta, 1971), 2·288 (1) and 2·301 (1) Å in bis(thiobiuretato)M^{II} (M = Pd, Pt) (Girling & Amma, 1976).

Within the thiocarbamic ligand, the C=S, C—O and C—N bonds around the trigonal carbon C(1) have partial double-bond character and the observed C=S, C—O and C—N distances agree with those found for other complexes of thiocarbamic esters (Bardi, Piazzesi, Del Pra, Celeste, Faraglia & Trincia, 1985; Bardi, Del Pra, Piazzesi & Berto, 1981).

The preparation of $[Pt(ETC)_4]I_2$ from PtI_2 and ETC in benzene requires a large excess of ligand, otherwise mixtures of 1:2 and 1:4 species are obtained. When the pale yellow 1:4 complex is dissolved in benzene, the solution turns immediately to orange red, owing to formation of the *trans* species.

The IR spectrum of *trans*-$[Pt(ETC)_2I_2]$ shows, in the ν(NH) region, a medium intensity band at 3258 cm^{-1}, whereas $[Pt(ETC)_4]I_2$ presents two equally intense absorptions at 3155 and 3108 cm^{-1}. The ν(NH) absorptions of coordinated ligand are at lower energy with respect to free ETC (3380 sh, 3270 *s* br cm^{-1}) following the general trend observed in the MTC and TC adducts. The ETC absorption at 1530 cm^{-1} (1550 sh cm^{-1}), assigned as mainly ν(CN) with a small δ(NH) contribution, shifts in the complexes at higher frequencies, as expected for ligand coordination through the S atom.

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Insertion of $Pt(PPh_3)_2$ into the Coordinated Thiadiphosphirene Ring: Structure of $[LCo\{P_2SPt(PPh_3)_2\}]BPh_4$, L = 1,1,1-Tris(diphenylphosphinomethyl)ethane

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Abstract. [1,2,3-η^3-4,4-di(triphenylphosphine)-1,2,3,4-thiadiphosphaplatinete][1,1,1-tris(diphenylphosphinomethyl)ethane]cobalt(I) tetraphenylborate, $[Co(C_{36}H_{30}P_4PtS)(C_{41}H_{39}P_3)][B(C_6H_5)_4]$, M_r = 1816·5, monoclinic, $P2_1$, a = 19·379 (11), b = 21·819 (12), c = 10·201 (8) Å, β = 98·66 (8)°, V = 4264 (5) Å^3, Z = 2, D_x = 1·414 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 20·5 cm^{-1}, $F(000)$ = 1852, room temperature, final R = 0·051 for 3508 observed reflections. Insertion of the $Pt(PPh_3)_2$ moiety into a bond of the P_2S ring coordinated to the cobalt atom in the $[LCo(P_2S)]^+$ cation essentially involves cleavage of that bond, which lengthens to 2·810 (8) Å. The tetraatomic metallacycle which is formed is highly puckered.

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Introduction. Triatomic rings formed by unsubstituted Group V and VI atoms coordinated to a metal centre provide potential sites for addition and insertion reactions. The insertion of appropriate metal–ligand systems (Di Vaira, Moneti, Peruzzini & Stoppioni, 1984) as well as of isolobal organic moieties (Di Vaira, Niccolai, Peruzzini & Stoppioni, 1985) into bonds of such rings has indeed recently been shown to occur. We expect to gain insight into the factors which favour these insertion processes by comparing the structures of related compounds differing from each other in the nature of the atoms which form the triatomic ring and/or in the nature of the metal atom involved in bond cleavage. As part of this study the structure of the present P_2S derivative has been determined and is compared with that of the isomorphous As_2S derivative previously reported (Di Vaira, Moneti, Peruzzini & Stoppioni, 1984).

Experimental. Red-brown prismatic crystals of the compound were obtained as previously described (Di Vaira, Moneti, Peruzzini & Stoppioni, 1984). Crystal dimensions 0·08 × 0·22 × 0·28 mm. Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions determined by least squares from settings of 24 reflections in the range $22 < 2\theta < 32°$. θ–2θ scan, 5740 unique reflections ($\pm h$, $+k$, $+l$) measured, $2\theta_{\max} = 44°$. Three standard reflections measured every 120 min; no significant variation. Intensities corrected for Lorentz and polarization factors and for absorption effects, using *SHELX*76 (Sheldrick, 1976); transmission factors 0·65–0·85. 3508 reflections with $I > 3\sigma(I)$ were considered observed. Structure refined assuming as initial values for the atomic coordinates those from the structure of the isomorphous As_2S derivative. Function minimized $\sum w(|F_o| - |F_c|)^2$; $w = 1/\sigma^2(F_o)$. Anisotropic thermal parameters applied to the Pt, Co, P and S sites and isotropic parameters (overall for each Ph group) to the C and B atoms. Rigid phenyl groups. H atoms in calculated positions [riding, rigid CH_3 group; C—H = 1·00 Å, U(H) = 1·2 U(C)]. The P and S occupancies of sites of the P_2S moiety could not be unambiguously assigned, although there was a slight indication, on the basis of R values and of trends in temperature factors from refinements performed on models with alternative sets of fixed P/S population parameters for the ring sites, that the S occupancy should be minimal for the site lying opposite the bond being cleaved. This site was finally assigned P character whereas each of the other two sites was assigned $\frac{1}{2}$P + $\frac{1}{2}$S occupancies on the basis of solution NMR data (Di Vaira, Moneti, Peruzzini & Stoppioni, 1984) and by analogy with the model used for the As_2S isomorph. With a total 229 parameters the refinement converged at $R = 0{\cdot}051$ and $wR = 0{\cdot}050$; $S = 1{\cdot}26$; $(\Delta/\sigma)_{\max} = 0{\cdot}05$, exclusive CH_3 shifts. Refinement of the enantiomeric structure under identical conditions converged at $R = 0{\cdot}058$ and $wR = 0{\cdot}057$. According to the R-factor test (Hamilton, 1965) this alternative configuration could be rejected at less than the 0·005 significance level, assuming no systematic errors in the data [$wR(2)/wR(1) = 1{\cdot}14$; $\mathscr{R}_{1,3279,0.005} \simeq 1{\cdot}002$]. Maximum and minimum height in the final difference Fourier synthesis 0·8 and $-0{\cdot}8$ e Å^{-3} respectively; scattering curves for neutral atoms and anomalous-dispersion correction terms from *International Tables for X-ray Crystallography* (1974).

Table 1. *Final positional parameters* ($\times 10^4$) *and isotropic thermal factors* ($\times 10^3$), *with e.s.d.'s in parentheses*

The y coordinate of Pt was not refined owing to the polar nature of the space group.

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

	x	y	z	$U_{\rm eq}/U_{\rm iso}$(Å^2)
Pt	2311 (1)	7000	2674 (1)	32 (1)
Co	2204 (1)	8652 (1)	2378 (2)	28 (1)
P(1)	3035 (3)	9381 (3)	2787 (5)	31 (1)
P(2)	1357 (3)	9345 (3)	2149 (5)	34 (1)
P(3)	2227 (3)	8651 (2)	194 (5)	29 (1)
P(4)†	1485 (3)	7807 (3)	2543 (6)	37 (1)
P(5)	2045 (3)	8215 (3)	4293 (5)	44 (1)
S†	2926 (3)	7883 (3)	3436 (5)	37 (1)
P(6)	3309 (3)	6383 (3)	3072 (6)	33 (1)
P(7)	1465 (4)	6270 (3)	1773 (7)	42 (1)
C(1)	2231 (9)	9982 (8)	552 (17)	30 (5)
C(2)	2723 (11)	10083 (9)	1854 (19)	49 (6)
C(3)	1464 (10)	9886 (9)	790 (20)	48 (6)
C(4)	2480 (10)	9422 (8)	−269 (18)	40 (5)
C(5)	2268 (11)	10565 (9)	−281 (21)	56 (6)
C(11)	3917 (7)	9251 (6)	2305 (11)	47 (2)
C(12)	4342 (7)	8818 (6)	3038 (11)	47 (2)
C(13)	4991 (7)	8671 (6)	2689 (11)	47 (2)
C(14)	5216 (7)	8959 (6)	1607 (11)	47 (2)
C(15)	4791 (7)	9393 (6)	874 (11)	47 (2)
C(16)	4142 (7)	9539 (6)	1223 (11)	47 (2)
C(21)	3321 (7)	9663 (5)	4494 (14)	54 (3)
C(22)	3379 (7)	9255 (5)	5558 (14)	54 (3)
C(23)	3603 (7)	9464 (5)	6844 (14)	54 (3)
C(24)	3769 (7)	10081 (5)	7066 (14)	54 (3)
C(25)	3711 (7)	10489 (5)	6002 (14)	54 (3)
C(26)	3487 (7)	10280 (5)	4716 (14)	54 (3)
C(31)	455 (7)	9075 (6)	1772 (12)	54 (3)
C(32)	39 (7)	9116 (6)	533 (12)	54 (3)
C(33)	−651 (7)	8914 (6)	370 (12)	54 (3)
C(34)	−927 (7)	8671 (6)	1446 (12)	54 (3)
C(35)	−512 (7)	8630 (6)	2684 (12)	54 (3)
C(36)	179 (7)	8832 (6)	2848 (12)	54 (3)
C(41)	1245 (6)	9867 (6)	3525 (10)	48 (3)
C(42)	721 (6)	10311 (6)	3362 (10)	48 (3)
C(43)	632 (6)	10698 (6)	4413 (10)	48 (3)
C(44)	1068 (6)	10641 (6)	5627 (10)	48 (3)
C(45)	1592 (6)	10197 (6)	5790 (10)	48 (3)
C(46)	1681 (6)	9810 (6)	4739 (10)	48 (3)
C(51)	1408 (7)	8513 (5)	−976 (14)	58 (3)
C(52)	1224 (7)	8878 (5)	−2097 (14)	58 (3)
C(53)	645 (7)	8725 (5)	−3024 (14)	58 (3)
C(54)	250 (7)	8208 (5)	−2829 (14)	58 (3)
C(55)	434 (7)	7843 (5)	−1708 (14)	58 (3)
C(56)	1013 (7)	7996 (5)	−781 (14)	58 (3)
C(61)	2855 (5)	8173 (5)	−540 (11)	44 (2)
C(62)	2723 (5)	8009 (5)	−1876 (11)	44 (2)
C(63)	3216 (5)	7671 (5)	−2437 (11)	44 (2)
C(64)	3841 (5)	7499 (5)	−1662 (11)	44 (2)
C(65)	3973 (5)	7663 (5)	−326 (11)	44 (2)
C(66)	3480 (5)	8000 (5)	235 (11)	44 (2)
C(71)	4131 (7)	6785 (6)	3490 (10)	52 (2)
C(72)	4654 (7)	6777 (6)	2687 (10)	52 (2)
C(73)	5295 (7)	7056 (6)	3119 (10)	52 (2)
C(74)	5415 (7)	7343 (6)	4354 (10)	52 (2)
C(75)	4893 (7)	7351 (6)	5157 (10)	52 (2)
C(76)	4251 (7)	7073 (6)	4725 (10)	52 (2)

† Sites with 0·5 P and 0·5 S population parameters.

Table 1 (*cont.*)

	x	*y*	*z*	U_{eq}/U_{iso}(Å^2)
C(81)	3433 (7)	5906 (6)	1670 (11)	55 (3)
C(82)	3607 (7)	5287 (6)	1807 (11)	55 (3)
C(83)	3646 (7)	4931 (6)	684 (11)	55 (3)
C(84)	3511 (7)	5194 (6)	−574 (11)	55 (3)
C(85)	3337 (7)	5813 (6)	−711 (11)	55 (3)
C(86)	3297 (7)	6170 (6)	412 (11)	55 (3)
C(91)	3394 (6)	5864 (6)	4470 (14)	55 (3)
C(92)	2793 (6)	5679 (6)	4961 (14)	55 (3)
C(93)	2819 (6)	5179 (6)	5820 (14)	55 (3)
C(94)	3445 (6)	4865 (6)	6189 (14)	55 (3)
C(95)	4046 (6)	5051 (6)	5699 (14)	55 (3)
C(96)	4020 (6)	5551 (6)	4839 (14)	55 (3)
C(101)	582 (9)	6535 (7)	1964 (13)	76 (3)
C(102)	61 (9)	6537 (7)	861 (13)	76 (3)
C(103)	−599 (9)	6771 (7)	966 (13)	76 (3)
C(104)	−737 (9)	7003 (7)	2174 (13)	76 (3)
C(105)	−215 (9)	7001 (7)	3278 (13)	76 (3)
C(106)	444 (9)	6767 (7)	3173 (13)	76 (3)
C(111)	1461 (7)	5486 (7)	2463 (16)	76 (3)
C(112)	1024 (7)	5327 (7)	3377 (16)	76 (3)
C(113)	1055 (7)	4738 (7)	3919 (16)	76 (3)
C(114)	1522 (7)	4309 (7)	3547 (16)	76 (3)
C(115)	1959 (7)	4468 (7)	2632 (16)	76 (3)
C(116)	1929 (7)	5057 (7)	2090 (16)	76 (3)
C(121)	1443 (7)	6131 (6)	−22 (15)	68 (3)
C(122)	1162 (7)	5600 (6)	−652 (15)	68 (3)
C(123)	1135 (7)	5533 (6)	−2019 (15)	68 (3)
C(124)	1390 (7)	5997 (6)	−2755 (15)	68 (3)
C(125)	1671 (7)	6528 (6)	−2126 (15)	68 (3)
C(126)	1698 (7)	6595 (6)	−759 (15)	68 (3)
C(131)	7490 (6)	7258 (6)	8480 (15)	62 (3)
C(132)	7537 (6)	6751 (6)	7666 (15)	62 (3)
C(133)	8115 (6)	6682 (6)	7010 (15)	62 (3)
C(134)	8644 (6)	7121 (6)	7167 (15)	62 (3)
C(135)	8596 (6)	7629 (6)	7981 (15)	62 (3)
C(136)	8019 (6)	7697 (6)	8637 (15)	62 (3)
C(141)	6327 (7)	7984 (6)	8309 (11)	52 (3)
C(142)	5692 (7)	8155 (6)	8689 (11)	52 (3)
C(143)	5273 (7)	8592 (6)	7954 (11)	52 (3)
C(144)	5488 (7)	8857 (6)	6839 (11)	52 (3)
C(145)	6123 (7)	8686 (6)	6459 (11)	52 (3)
C(146)	6542 (7)	8250 (6)	7194 (11)	52 (3)
C(151)	6196 (7)	6806 (6)	8934 (12)	56 (3)
C(152)	5931 (7)	6657 (6)	7624 (12)	56 (3)
C(153)	5391 (7)	6232 (6)	7354 (12)	56 (3)
C(154)	5114 (7)	5956 (6)	8394 (12)	56 (3)
C(155)	5379 (7)	6105 (6)	9704 (12)	56 (3)
C(156)	5919 (7)	6529 (6)	9973 (12)	56 (3)
C(161)	7033 (7)	7560 (6)	10752 (15)	77 (3)
C(162)	7274 (7)	7085 (6)	11618 (15)	77 (3)
C(163)	7481 (7)	7208 (6)	12962 (15)	77 (3)
C(164)	7447 (7)	7804 (6)	13440 (15)	77 (3)
C(165)	7206 (7)	8279 (6)	12573 (15)	77 (3)
C(166)	6999 (7)	8156 (6)	11229 (15)	77 (3)
B	6767 (12)	7402 (11)	9173 (22)	39 (6)

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

Pt···Co	3·620 (3)	Pt—P(4)	2·370 (6)
Pt—P(6)	2·341 (6)	Pt—P(7)	2·369 (7)
Pt—S	2·337 (6)	Co—P(1)	2·257 (6)
Co—P(2)	2·218 (6)	Co—P(3)	2·235 (5)
Co—P(4)	2·333 (7)	Co—P(5)	2·237 (6)
Co—S	2·342 (6)	P(4)—P(5)	2·138 (8)
P(5)—S	2·157 (8)	P(4)···S	2·810 (8)
P(4)—Pt—S	73·3 (2)	P(4)—Pt—P(6)	166·0 (2)
P(4)—Pt—P(7)	93·2 (2)	P(6)—Pt—S	92·8 (2)
P(6)—Pt—P(7)	100·7 (2)	P(7)—Pt—S	166·4 (2)
P(1)—Co—P(2)	92·0 (2)	P(1)—Co—P(3)	93·7 (2)
P(1)—Co—P(4)	164·0 (2)	P(1)—Co—P(5)	109·1 (2)
P(1)—Co—S	93·4 (2)	P(2)—Co—P(3)	91·2 (2)
P(2)—Co—P(4)	96·1 (2)	P(2)—Co—P(5)	100·7 (2)
P(2)—Co—S	156·7 (2)	P(3)—Co—P(4)	99·9 (2)
P(3)—Co—P(5)	153·7 (2)	P(3)—Co—S	111·0 (2)
P(4)—Co—P(5)	55·8 (2)	P(4)—Co—S	73·9 (2)
P(5)—Co—S	56·2 (2)	Pt—P(4)—Co	100·7 (2)
Pt—P(4)—P(5)	90·4 (3)	Co—P(4)—P(5)	59·8 (2)
Co—P(5)—P(4)	64·4 (2)	Co—P(5)—S	64·2 (2)
P(4)—P(5)—S	81·7 (3)	Pt—S—Co	101·4 (2)
Pt—S—P(5)	90·9 (2)	Co—S—P(5)	59·5 (2)

Sites P(4) and S have population parameters as described in Table 1.

Discussion. Atomic coordinates are given in Table 1.* Table 2 shows values of selected bond distances and angles. The structure consists of [*L*Co{P_2SPt(PPh_3)$_2$}]$^+$ cations and BPh_4^- anions. Fig. 1 shows a perspective view of the cation. The geometry of the cation is essentially similar to that of the As_2S analogue, with the Co atom surrounded by the P atoms of the tridentate phosphine ligand and by the atoms of the P_2S unit and the Pt atom in a nearly planar arrangement formed by two atoms of the latter unit and by the two PPh_3 phosphorus atoms. Although the orientational disorder of the triatomic unit, both in the present compound and in the As_2S analogue, poses some limitations on the significance of comparisons between the structures, the following points may be safely stated. All distances from the Co and Pt metal atoms to the sites of the P_2S group are consistently shorter, by 0·08–0·12 Å, than the corresponding distances in the As_2S derivative. A notable lengthening is undergone by the bond of the P_2S cycle where insertion occurs, approximately from the 2·12 (1) Å mean value detected for the parent [*L*Co(P_2S)]$^+$ cation (Di Vaira, Peruzzini & Stoppioni, 1984) to 2·810 (8) Å. However, the latter

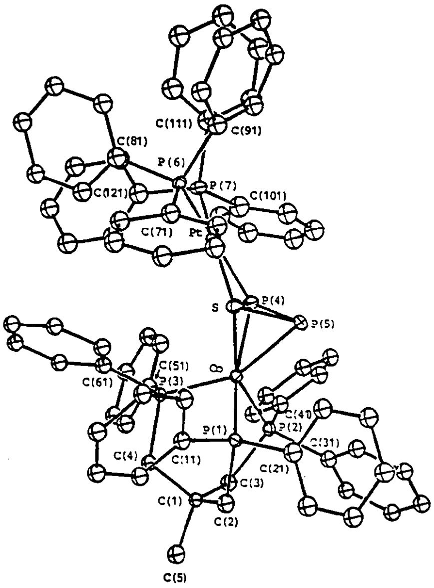

Fig. 1. Perspective view of the [*L*Co{P_2SPt(PPh_3)$_2$}]$^+$ cation. The first C atom of each phenyl group is labeled. The occupancies of P(4) and S sites are 0·5 P + 0·5 S (Johnson, 1976).

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* Anisotropic thermal parameters, H-atom coordinates, detailed bond lengths and angles and structure-factor lists have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43864 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distance is shorter than the corresponding one [3·03 (1) Å] found for the As_2S analogue, probably owing to the smaller overall size of the P_2S group. Actually, the latter group is more strained than the As_2S one after bond cleavage, as revealed by the value of the angle lying opposite the elongated bond in each unit [P_2S, 81·7 (3); As_2S, 80·4 (1)°]. The dihedral angle between the plane of the triatomic unit and the least-squares plane through the four atoms surrounding Pt, of 131·4 (3)°, does not differ considerably from that of 127·6 (3)° detected for the As_2S isomorph. We expect to obtain more information from additional compounds of this series.

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Structure and Chirality of $(-)_{546}$-Bis(2,4-pentanedionato)(3-formyl-2,4-pentanedionato)cobalt(III)

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Abstract. $[Co(C_5H_7O_2)_2(C_6H_7O_3)]$, $M_r = 384·27$, trigonal, $P3_221$, $a = 12·094\ (3)$, $c = 11·144\ (3)$ Å, $V = 1411·6\ (7)$ Å^3, $Z = 3$, $D_m = 1·35$, $D_x = 1·357$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0·7107$ Å, $\mu = 9·8$ cm^{-1}, $F(000) = 600$, $T \simeq 300$ K, final $R = 0·034$ for 1677 unique reflections. The (–) isomer has the Λ chirality and the Co atom is chelated in a distorted octahedron by the three ligands. Molecular symmetry contains a twofold axis parallel to the x axis: the formyl group is outside the plane of the formylate ligand (with twofold disorder) and is responsible for a perturbation in the chelate ring.

Introduction. The title compound was synthetized in an optically pure form by La Torre and is of interest as chiral chromatographic support (La Torre, Prosperi, Bonamico & Fares, 1985). The formyl group should affect the size of the 'twist angle' which is important in defining CD signal energies (Peacock, 1983); single-crystal CD spectra studies are in progress by Prosperi.

Here we report the determination by X-ray analysis of the structural chirality and the molecular structure of the (–) isomer of the formyl derivate of tris(2,4-pentanedionato)cobalt(III), $Co(pd)_3$.

Experimental. The crystals are black prisms, D_m by flotation. A specimen with dimensions *ca* 0·3 × 0·3 × 0·3 mm was selected for the intensity measurements and mounted on a Nicolet *P*3*m* computer-controlled four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell parameters were determined by least squares from the measured θ values of 15 selected reflections, θ range 11–17°. Intensities were measured in the θ–2θ scan mode. Two standard reflections (006 and 130) were re-measured after every 30 reflections: no significant loss in intensity throughout data collection. 6575 reflections were measured, $2\theta_{\max} = 55°$, 4590 with $I > 3\sigma(I)$ observed, index range $h = 0$ to 15, $k = -7$ to 7, $l = -14$ to 14. Intensities were corrected for Lorentz–polarization factors; semiempirical absorption correction, based on a 360° scan around the scattering vector of a pair of selected reflections, was applied: ratio between max. and min. values was 1·15; no other absorption correction was applied. 1677 independent reflections were obtained by averaging and merging equivalent reflections ($R_{\mathrm{int}} = 0·040$).

Structure was solved by Patterson and Fourier methods. Origin at 3_221. Subsequent difference Fourier maps revealed a twofold positional disorder for the formyl group (see later). The methyl H atoms were found to be disordered over two alternate staggered and eclipsed positions.

Positional and anisotropic thermal parameters for non-H atoms were refined by full-matrix least squares, minimizing $\sum w(|F_o| - k|F_c|)^2$, $w = 1/\sigma(F_o)^2$.

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