

# Crystal structures of bis[(9*S*,13*S*,14*S*)-3-methoxy-17-methylmorphinanium] tetrachloridocobaltate and tetrachloridocuprate

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**CCDC references:** 1522812; 1522811

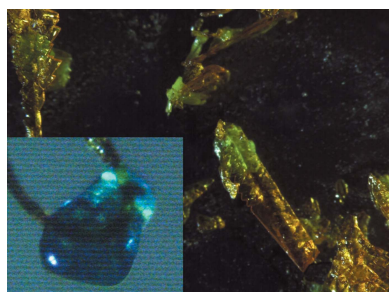
**Supporting information:** this article has supporting information at journals.iucr.org/e

(9*S*,13*S*,14*S*)-3-Methoxy-17-methylmorphinan (dextromethorphan) forms two isostructural salts with (a) tetrachloridocobaltate, namely bis[(9*S*,13*S*,14*S*)-3-methoxy-17-methylmorphinanium] tetrachloridocobaltate, (C<sub>18</sub>H<sub>26</sub>NO)<sub>2</sub>[CoCl<sub>4</sub>], and (b) tetrachloridocuprate, namely bis[(9*S*,13*S*,14*S*)-3-methoxy-17-methylmorphinanium] tetrachloridocuprate, (C<sub>18</sub>H<sub>26</sub>NO)<sub>2</sub>[CuCl<sub>4</sub>]. The distorted tetrahedral anions are located on twofold rotational axes. The dextromethorphan cation can be described as being composed of two ring systems, a tetrahydronaphthalene system *A+B* and a decahydroisoquinolinium subunit *C+D*, that are nearly perpendicular to one another: the angle between mean planes of the *A+B* and *C+D* moieties is 78.8 (1)° for (a) and 79.0 (1)° for (b). Two symmetry-related cations of protonated dextromethorphan are connected to the tetrachloridocobaltate (or tetrachloridocuprate) anions *via* strong N—H...Cl hydrogen bonds, forming neutral ion associates. These associates are packed in the (001) plane with no strong attractive bonding between them. Both compounds are attractive crystalline forms for unambiguous identification of the dextromethorphan and, presumably, of its optical isomer, levomethorphan.

## 1. Chemical context

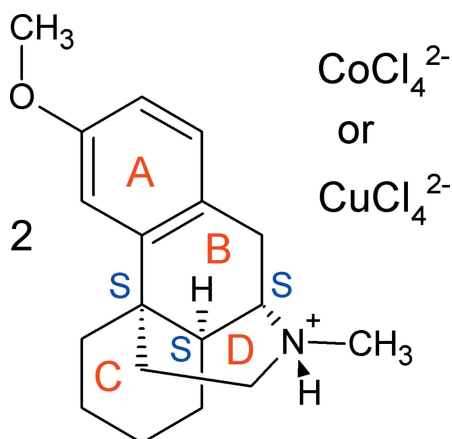
Seemingly innocuous and common over-the-counter drugs have a wide range of uses to treat illness and relieve pain, but they can also lead to long-term abuse and fatalities. Dextromethorphan (systematic name (9*S*,13*S*,14*S*)-3-methoxy-17-methylmorphinan) is a member of the *Morphinan* class of naturally occurring and semi-synthetic psychoactive drugs, chemically similar to morphine, codeine and oxycodone, and differing from these only by a few functional groups. It is commonly found in many cold and cough medicines. In high concentrations, dextromethorphan has effects similar to phencyclidine and ketamine, a dissociative anesthetic, which is known to induce visual hallucinations and a heightened sense of perceptual awareness (Bruera & Portenoy, 2010). The similarity to well-known substances of abuse that are highly controlled makes dextromethorphan an attractive target for recreational ingestion and purification from over-the-counter products.

Cobalt(II) compounds have been employed in color tests for alkaloid detection: *e.g.*, the Scott reagent (Cole, 2003). However, color reactions are usually not very specific and may lead to numerous false positives. To complicate the issue, levomethorphan, an optical isomer of dextromethorphan, is a strong opiate drug and is restricted like morphine in the US and many other countries. Therefore, usual NMR and MS



identification may be insufficient for clear identification of dextromethorphan and levomethorphan.

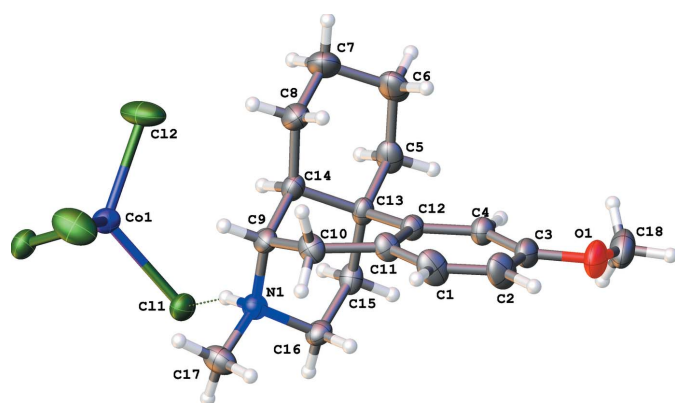
We suggest that easy-to-grow crystals of alkaloid metal complexes may provide a suitable analytical approach for unambiguous identification. As a part of this study, we report the crystal structures of two such compounds here.



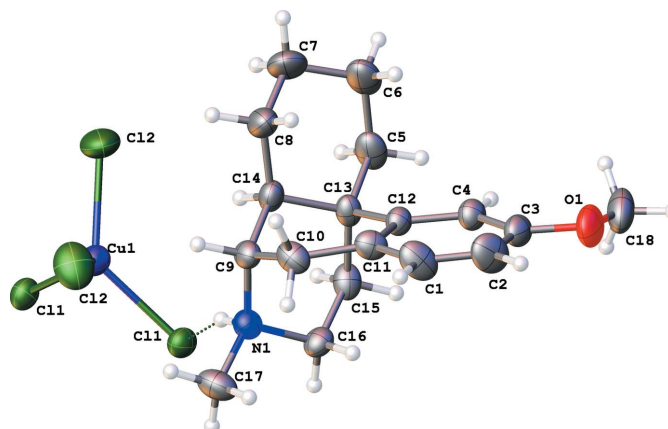
## 2. Structural commentary

The protonated dextromethorphan cations are nearly identical (Figs. 1–3). In both cases, protonation as well as interaction with the tetrachloridocobaltate or tetrachloridocuprate anions does not affect the geometry of the methorphan ring system (Fig. 4), leaving the shape of the organic molecule intact. The derived molecular dimensions within both structures are unexceptional and consistent with those known for similar molecules (Gylbert & Carlström, 1977).

There are four six-membered rings in a dextromethorphan molecule. The aromatic ring *A* is practically planar with deviations less than 0.01 Å in all cases. The cyclohexene ring *B* can be described as a half-chair shifted towards an envelope conformation: atoms C10, C11, C12 and C13 are adjacent to the aromatic ring and therefore almost planar while C9 and C14 deviate from this plane in opposite directions:



**Figure 1**  
The numbering scheme of the dextromethorphan tetrachloridocobaltate complex (*a*) with displacement ellipsoids drawn at the 50% probability level.

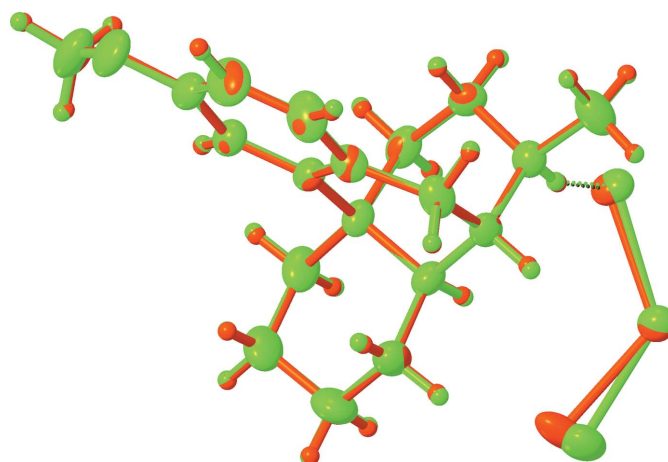


**Figure 2**  
The numbering scheme of the dextromethorphan tetrachloridocuprate complex (*b*) with displacement ellipsoids drawn at the 50% probability level.

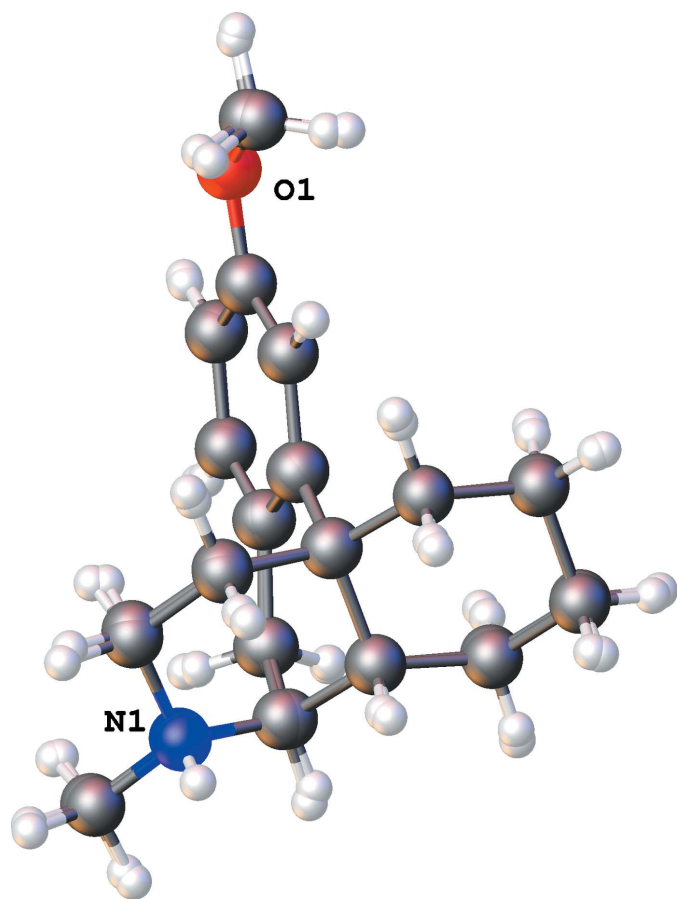
C9 = 0.191 (6) Å (*a*) and −0.173 (8) Å (*b*); C14 +0.553 (5) Å (*a*) and +0.562 (8) Å (*b*). This half-chair conformation is known (Ibberson *et al.*, 2008) for the unsubstituted cyclohexene molecule in the solid state.

The cyclohexane *C* and piperidine *B* rings both have chair conformations. These two rings are nearly coplanar, with the angles between their mean planes being 7.8 (1)° (*a*) and 8.2 (2)° (*b*). As a result, the dextromethorphan cation can be described as two ring systems *A+B* and *C+D*, being nearly perpendicular to each other: the angle between the mean planes of the *A+B* and *C+D* moieties is 78.8 (1)° for (*a*) and 79.0 (1)° for (*b*).

The tetrachloridocobaltate and tetrachloridocuprate anions both have a distorted tetrahedral geometry. In the cobalt complex, the C11–Co1–C12 angle is flattened to 116.59 (3)°, while in the copper analogue the C12–Cu1–C11 angle is 129.04 (4)°. The larger deviation from tetrahedral geometry in the copper(II) compound is possibly due to the Jahn–Teller effect, as packing effects should be similar in both compounds.



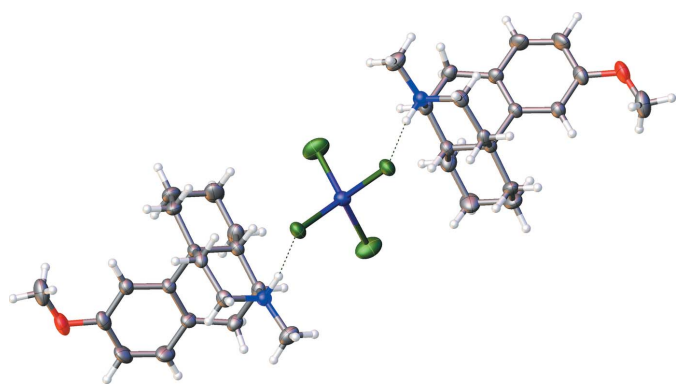
**Figure 3**  
Overlay of the dextromethorphan tetrachloridocobaltate (green) and tetrachloridocuprate (red) complexes.



**Figure 4**  
Overlay of the protonated dextromethorphan cation (*a*) and the dextromethorphan molecule (refcode XAPTAK01).

### 3. Supramolecular features

The tetrachloridocobaltate and tetrachloridocuprate anions are located on twofold rotational axes. Two identical protonated dextromethorphan cations are connected to tetrachloridocobaltate (or tetrachloridocuprate) anions *via* strong



**Figure 5**  
Two dextromethorphan cations forming an ion associate with the tetrachloridocobaltate dianion. Hydrogen bonds are drawn as dashed lines.

**Table 1**  
Hydrogen-bond geometry (Å, °) for (*a*).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···Cl1	0.93 (4)	2.26 (4)	3.145 (2)	158 (4)
C10–H10 <i>B</i> ···Cl2 <sup>i</sup>	0.97 (3)	2.71 (2)	3.609 (3)	153 (1)
C17–H17 <i>B</i> ···Cl2 <sup>ii</sup>	0.98 (3)	2.75 (3)	3.615 (4)	148 (1)

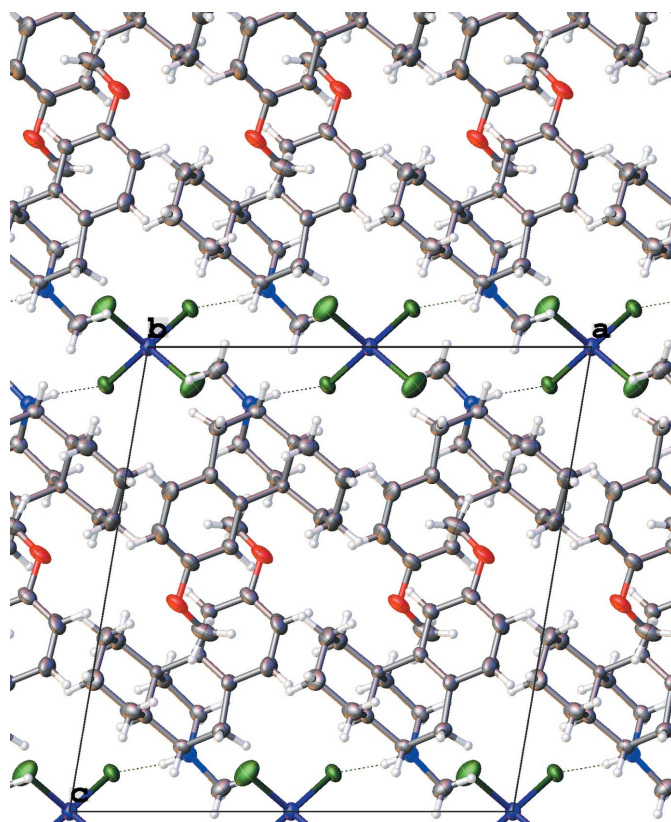
Symmetry codes: (i)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ ; (ii)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ .

**Table 2**  
Hydrogen-bond geometry (Å, °) for (*b*).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···Cl1	0.81 (6)	2.46 (6)	3.207 (4)	154 (5)
C10–H10 <i>A</i> ···Cl2 <sup>i</sup>	0.99	2.83	3.754 (5)	156
C17–H17 <i>B</i> ···Cl2 <sup>ii</sup>	0.98	2.68	3.590 (5)	156

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

N–H···Cl hydrogen bonds (Tables 1 and 2), thus forming neutral ion associates (Fig. 5). These associates are packed into layers in the (001) plane (Fig. 6) with no strong attractive bonding between them. Methyl groups adjacent to the protonated nitrogen atoms separate the tetrachloridometalate anions, thus reducing electrostatic repulsion between them. Close packing and electrostatic interaction with anion results in several short C–H···Cl contacts (Tables 1 and 2).



**Figure 6**  
Packing diagram of the ion associates in structure (*a*), viewed along [010].

**Table 3**  
Experimental details.

	(a)	(b)
<b>Crystal data</b>		
Chemical formula	(C <sub>18</sub> H <sub>26</sub> NO) <sub>2</sub> [CoCl <sub>4</sub> ]	(C <sub>18</sub> H <sub>26</sub> NO)[CuCl <sub>4</sub> ]
<i>M<sub>r</sub></i>	745.52	750.13
Crystal system, space group	Monoclinic, <i>C2</i>	Monoclinic, <i>C2</i>
Temperature (K)	173	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.8447 (6), 9.2316 (4), 14.7018 (6)	13.8066 (16), 9.2934 (12), 14.651 (3)
$\beta$ (°)	99.605 (2)	99.318 (6)
<i>V</i> (Å <sup>3</sup> )	1852.68 (14)	1855.1 (5)
<i>Z</i>	2	2
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.79	0.91
Crystal size (mm)	0.48 × 0.26 × 0.14	0.45 × 0.3 × 0.15
<b>Data collection</b>		
Diffractometer	Bruker PHOTON-100 CMOS	Bruker PHOTON-100 CMOS
Absorption correction	Multi-scan (SADABS, Bruker, 2015)	Multi-scan (SADABS, Bruker, 2015)
<i>T</i> <sub>min</sub> – <i>T</i> <sub>max</sub>	0.761, 0.979	0.714, 0.933
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	43153, 4803, 4183	31097, 4243, 3521
<i>R</i> <sub>int</sub>	0.061	0.047
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.677	0.649
<b>Refinement</b>		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.034, 0.083, 1.04	0.039, 0.100, 1.08
No. of reflections	4803	4243
No. of parameters	224	209
No. of restraints	1	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.50, -0.26	0.51, -0.33
Absolute structure	Flack <i>x</i> determined using 1711 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)	Flack <i>x</i> determined using 1463 quotients [( <i>I</i> <sup>+</sup> ) - ( <i>I</i> <sup>-</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>-</sup> )] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.000 (7)	-0.005 (6)

Computer programs: APEX2 and SAINT (Bruker, 2013), SHELXT (Sheldrick, 2015), SHELXS97 and SHELXL97 (Sheldrick, 2008) and OLEX2 (Dolomanov *et al.*, 2009).

The layers assemble in the 3D crystal (Fig. 6) *via* weak intermolecular forces: the only specific inter-layer contact is C15–H15B···O1 with C···O distances too long to be considered a strong hydrogen bond [3.473 (4) (a) and 3.507 (6) Å (b)].

#### 4. Database survey

There are three reported dextromethorphan structures deposited in the Cambridge Structural Database (CSD Version 5.37; Groom *et al.*, 2016). Of these structures, two report structures of the neutral molecule (refcodes XAPTAK and XAPTAK01), one of which (Swamy *et al.*, 2005) refers to a room-temperature measurement and the other (Scheins *et al.*, 2007) a high-quality charge-density investigation performed at 20 K.

A protonated form is also known in a form of the bromide salt (refcode DEXORP), in which one solvate water molecule is connected to a protonated nitrogen atom *via* a hydrogen bond (Gylbert & Carlström, 1977).

#### 5. Synthesis and crystallization

Dextromethorphan was isolated during the analysis of a proprietary cough syrup using a standard Pharmacopoeia

procedure (WHO, 2016). GC–MS assay of the hexane solution shows dextromethorphan to be a main component, with a small admixture of menthol.

Dextromethorphan was positively identified using NMR and FTIR spectra. Slow evaporation of a hexane solution at 274 K yields crystals which were also identified as dextromethorphan (refcode XAPTAK; Swamy *et al.*, 2005). Around 20 mg of the solid residue was treated with two drops of concentrated HCl and an excess of cobalt(II) chloride or copper(II) chloride. Overnight standing in a refrigerator yielded crystals of the title compounds. The colors of the resulting solids were characteristic with the tetrachloridocobaltate(II) salt being blue and the tetrachloridocuprate(II) salt yellow. The bright colors of the crystals make them easy to separate from possible crystalline impurities. We expect that levomethorphan would yield similar crystals with the opposite chirality.

Crystals suitable for X-ray investigation (Fig. 7) were cut from larger blocks before mounting on Mitigen loops.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. In (a), the hydrogen atom H1 of the protonated amine was refined in an isotropic approxima-

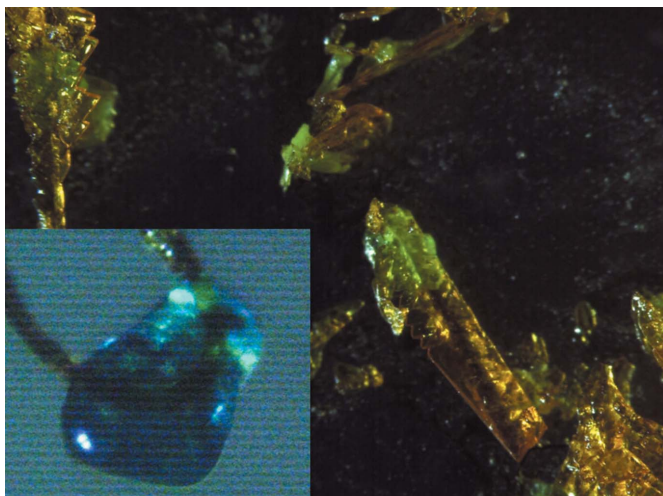
tion; idealized methyl groups refined as rotating groups with stretchable bonds and  $U_{\text{iso}} = 1.5U_{\text{iso}}(\text{C})$ ; all other hydrogen atoms were refined with riding coordinates and stretchable bonds with  $U_{\text{iso}} = 1.2U_{\text{iso}}(\text{C})$ . In (b), the hydrogen atoms were treated in a similar fashion.

### Acknowledgements

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**Figure 7**

Crystals of the dextromethorphan tetrachloridocobaltate (blue, left corner) and tetrachloridocuprate (yellow) salts. The diagonal image sizes are  $\sim 0.6$  and  $3$  mm, respectively.

## supporting information

*Acta Cryst.* (2017). E73, 63-67 [https://doi.org/10.1107/S2056989016019939]

## Crystal structures of bis[(9*S*,13*S*,14*S*)-3-methoxy-17-methylmorphinanium] tetrachloridocobaltate and tetrachloridocuprate

Eric Gauchat and Alexander Y. Nazarenko

### Computing details

For both compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013). Program(s) used to solve structure: *SHELXT* (Sheldrick, 2015) for a; *SHELXS97* (Sheldrick, 2008) for b. For both compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

### (a) Bis[(9*S*,13*S*,14*S*)-3-methoxy-17-methylmorphinanium] tetrachloridocobaltate

#### Crystal data

(C<sub>18</sub>H<sub>26</sub>NO)<sub>2</sub>[CoCl<sub>4</sub>]  
*M<sub>r</sub>* = 745.52  
 Monoclinic, *C*2  
*a* = 13.8447 (6) Å  
*b* = 9.2316 (4) Å  
*c* = 14.7018 (6) Å  
 $\beta$  = 99.605 (2)°  
*V* = 1852.68 (14) Å<sup>3</sup>  
*Z* = 2

*F*(000) = 786  
*D<sub>x</sub>* = 1.336 Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 9174 reflections  
 $\theta$  = 2.9–28.3°  
 $\mu$  = 0.79 mm<sup>-1</sup>  
*T* = 173 K  
 Plate, blue  
 0.48 × 0.26 × 0.14 mm

#### Data collection

Bruker PHOTON-100 CMOS  
 diffractometer  
 Radiation source: sealed tube  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS, Bruker, 2015)  
*T<sub>min</sub>* = 0.761, *T<sub>max</sub>* = 0.979  
 43153 measured reflections

4803 independent reflections  
 4183 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.061  
 $\theta_{\max}$  = 28.8°,  $\theta_{\min}$  = 2.8°  
*h* = -18→18  
*k* = -12→12  
*l* = -19→19

#### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.034  
*wR*(*F*<sup>2</sup>) = 0.083  
*S* = 1.04  
 4803 reflections  
 224 parameters  
 1 restraint  
 Hydrogen site location: mixed

H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.4319P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.50 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$   
 Absolute structure: Flack *x* determined using  
 1711 quotients [(*I*<sup>+</sup>)-(*I*)]/[(*I*<sup>+</sup>)+(*I*)] (Parsons *et al.*, 2013)  
 Absolute structure parameter: 0.000 (7)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.16362 (18)	0.6052 (3)	0.55317 (15)	0.0489 (6)
N1	0.25197 (17)	0.4294 (2)	0.12297 (15)	0.0277 (5)
C3	0.1767 (2)	0.6210 (3)	0.4633 (2)	0.0363 (7)
C4	0.2614 (2)	0.5804 (3)	0.43052 (18)	0.0302 (5)
H4	0.316 (2)	0.5398 (15)	0.4727 (15)	0.036*
C12	0.26809 (18)	0.5975 (3)	0.33709 (17)	0.0257 (5)
C11	0.1890 (2)	0.6534 (3)	0.27670 (18)	0.0295 (6)
C1	0.1055 (2)	0.6958 (4)	0.3114 (2)	0.0429 (7)
H1A	0.055 (2)	0.7347 (18)	0.2728 (17)	0.051*
C2	0.0990 (2)	0.6796 (5)	0.4031 (2)	0.0467 (8)
H2	0.037 (3)	0.7107 (14)	0.4268 (10)	0.056*
C18	0.2367 (3)	0.5315 (4)	0.6139 (2)	0.0544 (10)
H18A	0.2440 (18)	0.436 (3)	0.5914 (14)	0.082*
H18B	0.2184 (13)	0.526 (3)	0.6733 (18)	0.082*
H18C	0.2970 (18)	0.582 (2)	0.6180 (18)	0.082*
C10	0.1886 (2)	0.6676 (3)	0.17396 (18)	0.0320 (6)
H10A	0.1270 (16)	0.6305 (10)	0.1415 (9)	0.038*
H10B	0.1917 (2)	0.770 (3)	0.1590 (4)	0.038*
C9	0.2708 (2)	0.5904 (3)	0.13877 (18)	0.0277 (5)
H9	0.2785 (4)	0.6312 (16)	0.084 (2)	0.033*
C14	0.3669 (2)	0.6068 (3)	0.20608 (18)	0.0291 (5)
H14	0.4161 (19)	0.554 (2)	0.1814 (9)	0.035*
C8	0.3998 (3)	0.7643 (4)	0.2153 (2)	0.0424 (7)
H8A	0.3525 (15)	0.8185 (17)	0.2353 (6)	0.051*
H8B	0.4083 (3)	0.7987 (12)	0.1591 (17)	0.051*
C7	0.4956 (3)	0.7790 (5)	0.2833 (2)	0.0519 (9)
H7A	0.5481 (18)	0.7293 (17)	0.2587 (9)	0.062*
H7B	0.5132 (7)	0.881 (3)	0.2911 (3)	0.062*
C6	0.4853 (2)	0.7140 (5)	0.3763 (2)	0.0458 (8)
H6A	0.4353 (13)	0.7693 (15)	0.4036 (8)	0.055*
H6B	0.5490 (17)	0.7216 (5)	0.4192 (12)	0.055*
C5	0.4548 (2)	0.5556 (4)	0.36542 (19)	0.0374 (7)
H5A	0.4490 (2)	0.5175 (12)	0.4233 (17)	0.045*
H5B	0.5036 (14)	0.5032 (16)	0.3426 (6)	0.045*
C13	0.35654 (19)	0.5369 (3)	0.29939 (17)	0.0267 (5)
C15	0.33688 (19)	0.3737 (4)	0.28147 (16)	0.0297 (5)
H15A	0.3903 (14)	0.3325 (11)	0.2615 (5)	0.036*
H15B	0.3292 (3)	0.3292 (12)	0.3359 (14)	0.036*
C16	0.2462 (2)	0.3475 (3)	0.20999 (18)	0.0302 (6)

H16A	0.2401 (3)	0.248 (3)	0.1968 (4)	0.036*
H16B	0.1903 (15)	0.3772 (8)	0.2337 (7)	0.036*
C17	0.1662 (2)	0.3993 (4)	0.0495 (2)	0.0412 (7)
H17A	0.1063 (15)	0.427 (3)	0.0712 (9)	0.062*
H17B	0.1640 (12)	0.296 (3)	0.0350 (13)	0.062*
H17C	0.1725 (10)	0.455 (3)	−0.0055 (16)	0.062*
Co1	0.5000	0.37707 (5)	0.0000	0.02972 (14)
Cl1	0.41931 (5)	0.22074 (7)	0.08249 (4)	0.03266 (16)
Cl2	0.61476 (7)	0.52069 (9)	0.08226 (7)	0.0570 (3)
H1	0.306 (3)	0.389 (5)	0.102 (2)	0.045 (9)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0563 (15)	0.0602 (15)	0.0369 (11)	0.0015 (13)	0.0271 (10)	−0.0068 (11)
N1	0.0275 (11)	0.0271 (11)	0.0289 (11)	0.0014 (9)	0.0057 (9)	−0.0015 (8)
C3	0.0418 (16)	0.0377 (16)	0.0331 (14)	−0.0024 (13)	0.0173 (12)	−0.0085 (12)
C4	0.0307 (13)	0.0330 (14)	0.0279 (12)	0.0019 (12)	0.0083 (10)	−0.0013 (11)
C12	0.0254 (12)	0.0264 (12)	0.0267 (11)	0.0021 (11)	0.0079 (9)	−0.0019 (10)
C11	0.0274 (13)	0.0308 (14)	0.0306 (13)	0.0074 (11)	0.0054 (10)	−0.0041 (10)
C1	0.0319 (15)	0.0512 (19)	0.0450 (16)	0.0152 (14)	0.0048 (13)	−0.0101 (15)
C2	0.0362 (16)	0.060 (2)	0.0474 (17)	0.0076 (15)	0.0187 (14)	−0.0163 (16)
C18	0.083 (3)	0.049 (2)	0.0373 (17)	0.000 (2)	0.0278 (18)	0.0019 (15)
C10	0.0346 (14)	0.0312 (13)	0.0286 (12)	0.0069 (12)	0.0009 (11)	0.0000 (10)
C9	0.0344 (14)	0.0254 (12)	0.0236 (11)	−0.0031 (11)	0.0054 (10)	0.0037 (10)
C14	0.0279 (13)	0.0341 (14)	0.0271 (12)	−0.0018 (11)	0.0097 (10)	0.0007 (11)
C8	0.0501 (19)	0.0430 (18)	0.0353 (15)	−0.0152 (15)	0.0104 (13)	−0.0005 (13)
C7	0.0452 (19)	0.062 (2)	0.0488 (19)	−0.0242 (17)	0.0089 (15)	−0.0114 (17)
C6	0.0308 (15)	0.065 (2)	0.0392 (15)	−0.0089 (16)	−0.0003 (12)	−0.0110 (16)
C5	0.0239 (13)	0.057 (2)	0.0296 (13)	0.0048 (13)	0.0008 (11)	−0.0016 (13)
C13	0.0215 (12)	0.0371 (15)	0.0220 (11)	0.0024 (11)	0.0053 (9)	0.0004 (10)
C15	0.0332 (13)	0.0313 (13)	0.0259 (11)	0.0103 (13)	0.0089 (10)	0.0048 (12)
C16	0.0345 (14)	0.0242 (14)	0.0335 (13)	−0.0016 (11)	0.0108 (11)	0.0024 (10)
C17	0.0424 (16)	0.0376 (18)	0.0391 (15)	−0.0017 (14)	−0.0062 (12)	−0.0043 (13)
Co1	0.0263 (3)	0.0280 (3)	0.0351 (3)	0.000	0.0058 (2)	0.000
Cl1	0.0312 (3)	0.0354 (3)	0.0342 (3)	−0.0025 (3)	0.0137 (3)	−0.0038 (3)
Cl2	0.0577 (5)	0.0342 (4)	0.0711 (6)	−0.0164 (4)	−0.0130 (4)	0.0022 (4)

*Geometric parameters (Å, °)*

O1—C3	1.372 (3)	C14—C13	1.544 (4)
O1—C18	1.408 (5)	C8—H8A	0.91 (3)
N1—C9	1.520 (3)	C8—H8B	0.91 (3)
N1—C16	1.500 (3)	C8—C7	1.527 (5)
N1—C17	1.491 (3)	C7—H7A	0.98 (3)
N1—H1	0.93 (4)	C7—H7B	0.98 (3)
C3—C4	1.391 (4)	C7—C6	1.521 (5)
C3—C2	1.384 (5)	C6—H6A	1.00 (3)



C4—H4	0.97 (3)	C6—H6B	1.00 (3)
C4—C12	1.401 (3)	C6—C5	1.523 (6)
C12—C11	1.389 (4)	C5—H5A	0.94 (3)
C12—C13	1.532 (3)	C5—H5B	0.94 (3)
C11—C1	1.396 (4)	C5—C13	1.543 (4)
C11—C10	1.515 (4)	C13—C15	1.546 (4)
C1—H1A	0.90 (4)	C15—H15A	0.92 (2)
C1—C2	1.375 (5)	C15—H15B	0.92 (2)
C2—H2	1.02 (4)	C15—C16	1.516 (4)
C18—H18A	0.95 (3)	C16—H16A	0.94 (2)
C18—H18B	0.95 (3)	C16—H16B	0.94 (2)
C18—H18C	0.95 (3)	C17—H17A	0.97 (2)
C10—H10A	0.97 (2)	C17—H17B	0.97 (2)
C10—H10B	0.97 (2)	C17—H17C	0.97 (2)
C10—C9	1.506 (4)	Co1—C11 <sup>i</sup>	2.2920 (7)
C9—H9	0.91 (3)	Co1—C11	2.2921 (7)
C9—C14	1.527 (4)	Co1—C12 <sup>i</sup>	2.2592 (8)
C14—H14	0.96 (4)	Co1—C12	2.2591 (8)
C14—C8	1.523 (4)		
C3—O1—C18	117.8 (3)	H8A—C8—H8B	108.0
C9—N1—H1	109 (3)	C7—C8—H8A	109.5
C16—N1—C9	113.3 (2)	C7—C8—H8B	109.5
C16—N1—H1	104 (2)	C8—C7—H7A	109.5
C17—N1—C9	112.9 (2)	C8—C7—H7B	109.5
C17—N1—C16	112.0 (2)	H7A—C7—H7B	108.1
C17—N1—H1	106 (2)	C6—C7—C8	110.6 (3)
O1—C3—C4	124.0 (3)	C6—C7—H7A	109.5
O1—C3—C2	116.3 (3)	C6—C7—H7B	109.5
C2—C3—C4	119.7 (3)	C7—C6—H6A	109.6
C3—C4—H4	119.8	C7—C6—H6B	109.6
C3—C4—C12	120.4 (3)	C7—C6—C5	110.5 (3)
C12—C4—H4	119.8	H6A—C6—H6B	108.1
C4—C12—C13	120.1 (2)	C5—C6—H6A	109.6
C11—C12—C4	119.6 (2)	C5—C6—H6B	109.6
C11—C12—C13	119.8 (2)	C6—C5—H5A	109.2
C12—C11—C1	118.9 (3)	C6—C5—H5B	109.2
C12—C11—C10	122.7 (2)	C6—C5—C13	111.9 (3)
C1—C11—C10	118.3 (3)	H5A—C5—H5B	107.9
C11—C1—H1A	119.3	C13—C5—H5A	109.2
C2—C1—C11	121.4 (3)	C13—C5—H5B	109.2
C2—C1—H1A	119.3	C12—C13—C14	111.5 (2)
C3—C2—H2	120.1	C12—C13—C5	113.9 (2)
C1—C2—C3	119.9 (3)	C12—C13—C15	106.8 (2)
C1—C2—H2	120.1	C14—C13—C15	107.2 (2)
O1—C18—H18A	109.5	C5—C13—C14	108.0 (2)
O1—C18—H18B	109.5	C5—C13—C15	109.1 (2)
O1—C18—H18C	109.5	C13—C15—H15A	109.2

H18A—C18—H18B	109.5	C13—C15—H15B	109.2
H18A—C18—H18C	109.5	H15A—C15—H15B	107.9
H18B—C18—H18C	109.5	C16—C15—C13	112.1 (2)
C11—C10—H10A	108.5	C16—C15—H15A	109.2
C11—C10—H10B	108.5	C16—C15—H15B	109.2
H10A—C10—H10B	107.5	N1—C16—C15	110.8 (2)
C9—C10—C11	115.1 (2)	N1—C16—H16A	109.5
C9—C10—H10A	108.5	N1—C16—H16B	109.5
C9—C10—H10B	108.5	C15—C16—H16A	109.5
N1—C9—H9	108.3	C15—C16—H16B	109.5
N1—C9—C14	107.7 (2)	H16A—C16—H16B	108.1
C10—C9—N1	113.3 (2)	N1—C17—H17A	109.5
C10—C9—H9	108.3	N1—C17—H17B	109.5
C10—C9—C14	110.9 (2)	N1—C17—H17C	109.5
C14—C9—H9	108.3	H17A—C17—H17B	109.5
C9—C14—H14	107.5	H17A—C17—H17C	109.5
C9—C14—C13	109.5 (2)	H17B—C17—H17C	109.5
C8—C14—C9	111.5 (2)	Cl1 <sup>i</sup> —Co1—Cl1	101.95 (4)
C8—C14—H14	107.5	Cl2 <sup>i</sup> —Co1—Cl1	106.94 (3)
C8—C14—C13	113.0 (2)	Cl2—Co1—Cl1 <sup>i</sup>	106.94 (3)
C13—C14—H14	107.5	Cl2—Co1—Cl1	116.59 (3)
C14—C8—H8A	109.5	Cl2 <sup>i</sup> —Co1—Cl1 <sup>i</sup>	116.59 (3)
C14—C8—H8B	109.5	Cl2—Co1—Cl2 <sup>i</sup>	108.13 (5)
C14—C8—C7	110.9 (3)		
O1—C3—C4—C12	178.7 (3)	C10—C9—C14—C13	61.9 (3)
O1—C3—C2—C1	-178.5 (3)	C9—N1—C16—C15	-54.1 (3)
N1—C9—C14—C8	171.6 (2)	C9—C14—C8—C7	179.6 (2)
N1—C9—C14—C13	-62.6 (3)	C9—C14—C13—C12	-54.0 (3)
C3—C4—C12—C11	-1.0 (4)	C9—C14—C13—C5	-180.0 (2)
C3—C4—C12—C13	-173.0 (3)	C9—C14—C13—C15	62.5 (3)
C4—C3—C2—C1	0.7 (5)	C14—C8—C7—C6	-55.7 (4)
C4—C12—C11—C1	2.2 (4)	C14—C13—C15—C16	-57.8 (3)
C4—C12—C11—C10	-176.6 (3)	C8—C14—C13—C12	71.0 (3)
C4—C12—C13—C14	-162.0 (2)	C8—C14—C13—C5	-55.0 (3)
C4—C12—C13—C5	-39.4 (4)	C8—C14—C13—C15	-172.5 (2)
C4—C12—C13—C15	81.2 (3)	C8—C7—C6—C5	57.4 (4)
C12—C11—C1—C2	-1.9 (5)	C7—C6—C5—C13	-59.0 (4)
C12—C11—C10—C9	11.7 (4)	C6—C5—C13—C12	-68.1 (3)
C12—C13—C15—C16	61.8 (3)	C6—C5—C13—C14	56.4 (3)
C11—C12—C13—C14	26.0 (4)	C6—C5—C13—C15	172.6 (2)
C11—C12—C13—C5	148.6 (3)	C5—C13—C15—C16	-174.6 (2)
C11—C12—C13—C15	-90.8 (3)	C13—C12—C11—C1	174.2 (3)
C11—C1—C2—C3	0.4 (6)	C13—C12—C11—C10	-4.6 (4)
C11—C10—C9—N1	81.1 (3)	C13—C14—C8—C7	55.7 (3)
C11—C10—C9—C14	-40.1 (3)	C13—C15—C16—N1	53.7 (3)
C1—C11—C10—C9	-167.1 (3)	C16—N1—C9—C10	-64.7 (3)
C2—C3—C4—C12	-0.4 (5)	C16—N1—C9—C14	58.4 (3)

C18—O1—C3—C4	−6.0 (5)	C17—N1—C9—C10	63.9 (3)
C18—O1—C3—C2	173.2 (3)	C17—N1—C9—C14	−173.0 (2)
C10—C11—C1—C2	176.9 (3)	C17—N1—C16—C15	176.9 (2)
C10—C9—C14—C8	−63.9 (3)		

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1 $\cdots$ C11	0.93 (4)	2.26 (4)	3.145 (2)	158 (4)
C10—H10B $\cdots$ C12 <sup>ii</sup>	0.97 (3)	2.71 (2)	3.609 (3)	153 (1)
C17—H17B $\cdots$ C12 <sup>iii</sup>	0.98 (3)	2.75 (3)	3.615 (4)	148 (1)

Symmetry codes: (ii)  $x-1/2, y+1/2, z$ ; (iii)  $x-1/2, y-1/2, z$ .

#### (b) Bis[(9S,13S,14S)-3-methoxy-17-methylmorphinanium] tetrachloridocuprate

##### Crystal data

(C<sub>18</sub>H<sub>26</sub>NO)[CuCl<sub>4</sub>]  
 $M_r = 750.13$   
 Monoclinic, C2  
 $a = 13.8066$  (16)  $\text{\AA}$   
 $b = 9.2934$  (12)  $\text{\AA}$   
 $c = 14.651$  (3)  $\text{\AA}$   
 $\beta = 99.318$  (6) $^\circ$   
 $V = 1855.1$  (5)  $\text{\AA}^3$   
 $Z = 2$

$F(000) = 790$   
 $D_x = 1.343$  Mg m<sup>−3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$   
 Cell parameters from 1064 reflections  
 $\theta = 3.1\text{--}24.8^\circ$   
 $\mu = 0.91$  mm<sup>−1</sup>  
 $T = 173$  K  
 Plate, yellow  
 $0.45 \times 0.3 \times 0.15$  mm

##### Data collection

Bruker PHOTON-100 CMOS  
 diffractometer  
 Radiation source: sealedtube  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS, Bruker, 2015)  
 $T_{\min} = 0.714$ ,  $T_{\max} = 0.933$   
 31097 measured reflections

4243 independent reflections  
 3521 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.047$   
 $\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.8^\circ$   
 $h = -17 \rightarrow 17$   
 $k = -12 \rightarrow 12$   
 $l = -19 \rightarrow 19$

##### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.100$   
 $S = 1.08$   
 4243 reflections  
 209 parameters  
 1 restraint  
 Hydrogen site location: mixed

H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 1.3109P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.51$  e  $\text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.33$  e  $\text{\AA}^{-3}$   
 Absolute structure: Flack  $x$  determined using  
 1463 quotients  $[(I^+)-(I^-)]/[(I^+)+(I^-)]$  (Parsons et  
 al., 2013)  
 Absolute structure parameter:  $-0.005$  (6)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.1671 (3)	0.6033 (4)	0.5575 (2)	0.0560 (9)
N1	0.2499 (3)	0.4329 (4)	0.1218 (2)	0.0329 (8)
H1	0.296 (4)	0.402 (6)	0.100 (4)	0.049*
C1	0.1031 (3)	0.6887 (6)	0.3155 (4)	0.0497 (12)
H1A	0.0477	0.7261	0.2756	0.060*
C2	0.0989 (4)	0.6737 (7)	0.4073 (4)	0.0535 (13)
H2	0.0413	0.7018	0.4304	0.064*
C3	0.1774 (3)	0.6181 (5)	0.4669 (3)	0.0400 (10)
C4	0.2621 (3)	0.5790 (5)	0.4319 (3)	0.0340 (9)
H4	0.3167	0.5404	0.4723	0.041*
C5	0.4546 (3)	0.5603 (6)	0.3624 (3)	0.0456 (12)
H5A	0.4499	0.5191	0.4239	0.055*
H5B	0.5064	0.5072	0.3369	0.055*
C6	0.4833 (4)	0.7196 (7)	0.3735 (3)	0.0562 (14)
H6A	0.4333	0.7725	0.4016	0.067*
H6B	0.5471	0.7288	0.4150	0.067*
C7	0.4911 (4)	0.7841 (7)	0.2798 (4)	0.0639 (16)
H7A	0.5438	0.7347	0.2535	0.077*
H7B	0.5085	0.8872	0.2873	0.077*
C8	0.3941 (4)	0.7686 (6)	0.2138 (3)	0.0506 (13)
H8A	0.3426	0.8246	0.2376	0.061*
H8B	0.4014	0.8078	0.1524	0.061*
C9	0.2665 (3)	0.5938 (4)	0.1385 (3)	0.0325 (9)
H9	0.2729	0.6402	0.0781	0.039*
C10	0.1834 (3)	0.6653 (5)	0.1759 (3)	0.0374 (9)
H10A	0.1834	0.7690	0.1604	0.045*
H10B	0.1208	0.6242	0.1441	0.045*
C11	0.1865 (3)	0.6506 (4)	0.2785 (3)	0.0335 (9)
C12	0.2669 (3)	0.5965 (4)	0.3383 (3)	0.0287 (8)
C13	0.3559 (3)	0.5401 (5)	0.2980 (3)	0.0313 (9)
C14	0.3634 (3)	0.6116 (5)	0.2038 (3)	0.0340 (9)
H14	0.4149	0.5590	0.1763	0.041*
C15	0.3388 (3)	0.3775 (5)	0.2790 (3)	0.0364 (9)
H15A	0.3966	0.3365	0.2562	0.044*
H15B	0.3322	0.3283	0.3376	0.044*
C16	0.2482 (3)	0.3492 (5)	0.2089 (3)	0.0349 (9)
H16A	0.2440	0.2451	0.1943	0.042*
H16B	0.1893	0.3761	0.2356	0.042*
C17	0.1634 (4)	0.4004 (5)	0.0501 (3)	0.0492 (12)

H17A	0.1031	0.4261	0.0736	0.074*
H17B	0.1625	0.2975	0.0355	0.074*
H17C	0.1676	0.4562	-0.0058	0.074*
C18	0.2410 (5)	0.5329 (7)	0.6180 (4)	0.0624 (16)
H18A	0.2501	0.4356	0.5950	0.094*
H18B	0.2222	0.5270	0.6796	0.094*
H18C	0.3026	0.5868	0.6218	0.094*
Cu1	0.5000	0.36997 (7)	0.0000	0.0369 (2)
Cl1	0.41472 (7)	0.21415 (11)	0.07511 (7)	0.0354 (2)
Cl2	0.62112 (11)	0.51975 (14)	0.05807 (10)	0.0632 (4)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.068 (2)	0.066 (2)	0.043 (2)	0.0020 (19)	0.0321 (18)	-0.0075 (17)
N1	0.0336 (19)	0.0322 (17)	0.0332 (19)	0.0029 (15)	0.0062 (15)	-0.0022 (15)
C1	0.036 (2)	0.059 (3)	0.053 (3)	0.017 (2)	0.005 (2)	-0.014 (2)
C2	0.036 (2)	0.067 (3)	0.061 (3)	0.010 (2)	0.020 (2)	-0.016 (3)
C3	0.047 (3)	0.040 (2)	0.038 (2)	-0.003 (2)	0.020 (2)	-0.0082 (19)
C4	0.036 (2)	0.035 (2)	0.033 (2)	0.0031 (17)	0.0112 (17)	-0.0017 (17)
C5	0.027 (2)	0.073 (4)	0.036 (2)	0.004 (2)	-0.0010 (17)	-0.002 (2)
C6	0.036 (2)	0.087 (4)	0.044 (3)	-0.013 (3)	0.000 (2)	-0.011 (3)
C7	0.052 (3)	0.075 (4)	0.064 (4)	-0.034 (3)	0.011 (3)	-0.012 (3)
C8	0.059 (3)	0.055 (3)	0.038 (3)	-0.023 (2)	0.008 (2)	0.001 (2)
C9	0.039 (2)	0.031 (2)	0.027 (2)	-0.0030 (17)	0.0024 (16)	0.0040 (16)
C10	0.039 (2)	0.034 (2)	0.036 (2)	0.0091 (18)	-0.0027 (18)	-0.0012 (18)
C11	0.027 (2)	0.032 (2)	0.042 (2)	0.0062 (16)	0.0047 (17)	-0.0049 (18)
C12	0.0298 (19)	0.0282 (19)	0.030 (2)	0.0030 (16)	0.0097 (16)	-0.0006 (16)
C13	0.0249 (19)	0.043 (2)	0.027 (2)	0.0045 (17)	0.0049 (15)	0.0007 (18)
C14	0.033 (2)	0.041 (2)	0.029 (2)	-0.0017 (18)	0.0101 (17)	0.0025 (18)
C15	0.041 (2)	0.036 (2)	0.034 (2)	0.015 (2)	0.0109 (16)	0.004 (2)
C16	0.039 (2)	0.028 (2)	0.039 (2)	0.0003 (17)	0.0110 (17)	0.0042 (18)
C17	0.052 (3)	0.041 (3)	0.049 (3)	-0.002 (2)	-0.008 (2)	-0.008 (2)
C18	0.099 (5)	0.054 (3)	0.041 (3)	0.002 (3)	0.033 (3)	0.006 (3)
Cu1	0.0381 (4)	0.0337 (4)	0.0402 (4)	0.000	0.0105 (3)	0.000
Cl1	0.0329 (5)	0.0376 (5)	0.0381 (5)	-0.0018 (4)	0.0126 (4)	-0.0028 (4)
Cl2	0.0780 (10)	0.0484 (7)	0.0639 (8)	-0.0284 (7)	0.0131 (7)	-0.0041 (6)

*Geometric parameters (Å, °)*

O1—C3	1.366 (5)	C9—H9	1.0000
O1—C18	1.401 (7)	C9—C10	1.504 (6)
N1—H1	0.81 (5)	C9—C14	1.523 (6)
N1—C9	1.526 (5)	C10—H10A	0.9900
N1—C16	1.499 (5)	C10—H10B	0.9900
N1—C17	1.487 (6)	C10—C11	1.503 (6)
C1—H1A	0.9500	C11—C12	1.392 (6)
C1—C2	1.363 (7)	C12—C13	1.539 (5)

C1—C11	1.395 (6)	C13—C14	1.551 (6)
C2—H2	0.9500	C13—C15	1.548 (7)
C2—C3	1.377 (7)	C14—H14	1.0000
C3—C4	1.398 (6)	C15—H15A	0.9900
C4—H4	0.9500	C15—H15B	0.9900
C4—C12	1.394 (6)	C15—C16	1.507 (6)
C5—H5A	0.9900	C16—H16A	0.9900
C5—H5B	0.9900	C16—H16B	0.9900
C5—C6	1.535 (9)	C17—H17A	0.9800
C5—C13	1.538 (6)	C17—H17B	0.9800
C6—H6A	0.9900	C17—H17C	0.9800
C6—H6B	0.9900	C18—H18A	0.9800
C6—C7	1.517 (8)	C18—H18B	0.9800
C7—H7A	0.9900	C18—H18C	0.9800
C7—H7B	0.9900	Cu1—C11 <sup>i</sup>	2.2615 (11)
C7—C8	1.526 (7)	Cu1—C11	2.2614 (11)
C8—H8A	0.9900	Cu1—C12	2.2354 (13)
C8—H8B	0.9900	Cu1—C12 <sup>i</sup>	2.2354 (13)
C8—C14	1.519 (6)		
C3—O1—C18	118.8 (4)	C11—C10—C9	115.1 (3)
C9—N1—H1	108 (4)	C11—C10—H10A	108.5
C16—N1—H1	106 (4)	C11—C10—H10B	108.5
C16—N1—C9	113.3 (3)	C1—C11—C10	118.2 (4)
C17—N1—H1	104 (4)	C12—C11—C1	118.1 (4)
C17—N1—C9	113.3 (3)	C12—C11—C10	123.6 (4)
C17—N1—C16	112.0 (3)	C4—C12—C13	120.4 (3)
C2—C1—H1A	119.1	C11—C12—C4	120.1 (4)
C2—C1—C11	121.8 (4)	C11—C12—C13	119.1 (4)
C11—C1—H1A	119.1	C5—C13—C12	114.0 (3)
C1—C2—H2	119.7	C5—C13—C14	108.3 (3)
C1—C2—C3	120.6 (4)	C5—C13—C15	108.9 (4)
C3—C2—H2	119.7	C12—C13—C14	111.6 (3)
O1—C3—C2	117.3 (4)	C12—C13—C15	107.0 (3)
O1—C3—C4	123.7 (4)	C15—C13—C14	106.8 (3)
C2—C3—C4	119.0 (4)	C8—C14—C9	111.6 (4)
C3—C4—H4	119.8	C8—C14—C13	112.5 (4)
C12—C4—C3	120.4 (4)	C8—C14—H14	107.7
C12—C4—H4	119.8	C9—C14—C13	109.5 (3)
H5A—C5—H5B	107.9	C9—C14—H14	107.7
C6—C5—H5A	109.3	C13—C14—H14	107.7
C6—C5—H5B	109.3	C13—C15—H15A	109.1
C6—C5—C13	111.7 (4)	C13—C15—H15B	109.1
C13—C5—H5A	109.3	H15A—C15—H15B	107.9
C13—C5—H5B	109.3	C16—C15—C13	112.3 (3)
C5—C6—H6A	109.7	C16—C15—H15A	109.1
C5—C6—H6B	109.7	C16—C15—H15B	109.1
H6A—C6—H6B	108.2	N1—C16—C15	111.4 (3)

C7—C6—C5	109.9 (4)	N1—C16—H16A	109.4
C7—C6—H6A	109.7	N1—C16—H16B	109.4
C7—C6—H6B	109.7	C15—C16—H16A	109.4
C6—C7—H7A	109.5	C15—C16—H16B	109.4
C6—C7—H7B	109.5	H16A—C16—H16B	108.0
C6—C7—C8	110.7 (4)	N1—C17—H17A	109.5
H7A—C7—H7B	108.1	N1—C17—H17B	109.5
C8—C7—H7A	109.5	N1—C17—H17C	109.5
C8—C7—H7B	109.5	H17A—C17—H17B	109.5
C7—C8—H8A	109.5	H17A—C17—H17C	109.5
C7—C8—H8B	109.5	H17B—C17—H17C	109.5
H8A—C8—H8B	108.1	O1—C18—H18A	109.5
C14—C8—C7	110.8 (5)	O1—C18—H18B	109.5
C14—C8—H8A	109.5	O1—C18—H18C	109.5
C14—C8—H8B	109.5	H18A—C18—H18B	109.5
N1—C9—H9	108.3	H18A—C18—H18C	109.5
C10—C9—N1	112.8 (3)	H18B—C18—H18C	109.5
C10—C9—H9	108.3	Cl1—Cu1—Cl1 <sup>i</sup>	100.36 (6)
C10—C9—C14	111.6 (3)	Cl2—Cu1—Cl1 <sup>i</sup>	99.65 (5)
C14—C9—N1	107.5 (3)	Cl2 <sup>i</sup> —Cu1—Cl1	99.65 (5)
C14—C9—H9	108.3	Cl2 <sup>i</sup> —Cu1—Cl1 <sup>i</sup>	129.04 (4)
C9—C10—H10A	108.5	Cl2—Cu1—Cl1	129.04 (4)
C9—C10—H10B	108.5	Cl2 <sup>i</sup> —Cu1—Cl2	102.97 (9)
H10A—C10—H10B	107.5		
O1—C3—C4—C12	179.5 (4)	C9—C10—C11—C1	-167.6 (4)
N1—C9—C10—C11	82.2 (4)	C9—C10—C11—C12	10.2 (6)
N1—C9—C14—C8	171.7 (3)	C10—C9—C14—C8	-64.1 (5)
N1—C9—C14—C13	-63.0 (4)	C10—C9—C14—C13	61.2 (5)
C1—C2—C3—O1	-178.6 (5)	C10—C11—C12—C4	-176.6 (4)
C1—C2—C3—C4	0.9 (8)	C10—C11—C12—C13	-3.6 (6)
C1—C11—C12—C4	1.2 (6)	C11—C1—C2—C3	-0.8 (9)
C1—C11—C12—C13	174.2 (4)	C11—C12—C13—C5	148.6 (4)
C2—C1—C11—C10	177.7 (5)	C11—C12—C13—C14	25.5 (5)
C2—C1—C11—C12	-0.2 (7)	C11—C12—C13—C15	-91.0 (4)
C2—C3—C4—C12	0.1 (7)	C12—C13—C14—C8	71.2 (5)
C3—C4—C12—C11	-1.2 (6)	C12—C13—C14—C9	-53.6 (5)
C3—C4—C12—C13	-174.1 (4)	C12—C13—C15—C16	61.9 (4)
C4—C12—C13—C5	-38.4 (6)	C13—C5—C6—C7	-59.2 (6)
C4—C12—C13—C14	-161.5 (4)	C13—C15—C16—N1	53.3 (4)
C4—C12—C13—C15	82.0 (4)	C14—C9—C10—C11	-39.0 (5)
C5—C6—C7—C8	58.2 (6)	C14—C13—C15—C16	-57.7 (4)
C5—C13—C14—C8	-55.1 (5)	C15—C13—C14—C8	-172.2 (4)
C5—C13—C14—C9	-179.8 (4)	C15—C13—C14—C9	63.1 (4)
C5—C13—C15—C16	-174.4 (3)	C16—N1—C9—C10	-65.5 (4)
C6—C5—C13—C12	-68.5 (5)	C16—N1—C9—C14	58.0 (4)
C6—C5—C13—C14	56.3 (5)	C17—N1—C9—C10	63.5 (5)
C6—C5—C13—C15	172.1 (4)	C17—N1—C9—C14	-173.1 (3)

C6—C7—C8—C14	-57.0 (6)	C17—N1—C16—C15	177.1 (4)
C7—C8—C14—C9	179.7 (4)	C18—O1—C3—C2	173.1 (5)
C7—C8—C14—C13	56.1 (5)	C18—O1—C3—C4	-6.3 (7)
C9—N1—C16—C15	-53.3 (5)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...C11	0.81 (6)	2.46 (6)	3.207 (4)	154 (5)
C10—H10A...C12 <sup>ii</sup>	0.99	2.83	3.754 (5)	156
C17—H17B...C12 <sup>iii</sup>	0.98	2.68	3.590 (5)	156

Symmetry codes: (ii)  $x-1/2, y+1/2, z$ ; (iii)  $x-1/2, y-1/2, z$ .