rate (Mak *et al.*, 1976) the two H atoms of H_2S could not be detected. In the light of the present results it seems reasonable that the H_2S is also rotationally disordered about [001] to lie in the surface of a double cone with S at the common apex. Since H_2S is not linear the cone will be flatter than the HCl cone and, as observed, both the *a* and *c* cell constants should be larger in the H_2S clathrate.

We thank R. G. Copperthwaite for growing the crystals, G. Gafner for assistance with the X-ray data collection and H. W. W. Adrian for operating the neutron diffractometer.

References

COPPERTHWAITE, R. G. (1976). *Chem. Commun.* pp. 707–709.

International Tables for X-ray Crystallography (1968). Vol. III, p. 268. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 270. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MAK, T. C. W., TSE, J. S., TSE, C., LEE, K. & CHONG, Y. (1976). *J. Chem. Soc. Perkin* II, pp. 1169–1172.

PALIN, D. W. & POWELL, H. M. (1947). *J. Chem. Soc.* pp. 208–221.

SHELDRICK, G. M. (1976). Private communication.

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Mixed-Ligand Complexes in K_2ReCl_6–K_2ReBr_6 Solid Solution

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K_2ReCl_6 and K_2ReBr_6 form a complete solid solution between 420°C and the melting point at 715–730°C by equilibration with the gas phase. The average Re–*X* length changes continuously from 2·35 Å (K_2ReCl_6) to 2·51 Å (K_2ReBr_6) with a considerable variation of the valence force constant as determined by X-ray diffraction and FIR spectroscopy. The mixed-ligand complexes can be dissolved in aqueous solution and separated chemically. The ligands are distributed randomly, as expected for compounds with weak covalent bonding, with a minimum of short-range order at the 1:1 composition of the solid solution.

Introduction

The crystal structure of coordination compounds in general depends on the type of bonding and the site symmetry of the complexes. Octahedrally coordinated compounds often possess cubic, tetragonal or hexagonal symmetry. If two complexes with different ligands form a solid solution, the symmetry of the complexes and of the crystal structure can change in three different ways: (1) The ligands of the complexes are distributed randomly with a maximum of entropy. All kinds of mixed-ligand complexes coexist without a long-range order. (2) One special configuration of ligands is formed preferentially, but no orientation relative to the other complexes exists. (3) The mixed-ligand complex with one particular configuration has a long-range order, thus forming a superlattice. In this case the solid solution is restricted to certain compositions.

The random orientation of different ligands is often encountered in compounds with ionic bonds such as KCl–KBr solid solution (ss) (Wasastjerna, 1946). With increasing covalency the second and third kind of ordering is preferred. In K_2ReCl_6–K_2ReBr_6 ss, obtained by coprecipitation from aqueous solution, the $ReCl_6$ and $ReBr_6$ octahedra are randomly distributed in the cubic K_2PtCl_6 structure (Müller, 1963). In $K_2[OsO_2Cl_4]$ the anions are ordered in a tetragonally distorted K_2PtCl_6 structure (Kruse, 1961). The third kind of ordering can be determined by X-ray or neutron diffraction. The second possibility can often be studied by spectroscopic methods characterizing the short-range order, such as infrared or electron spectroscopy (e.g. Jørgensen, Preetz & Homborg, 1971). This method, however, becomes more tedious if the solid solution contains several different mixed-ligand complexes with overlapping spectra. Mixed-ligand complexes with very weak covalent bonding, in general, cannot be separated chemically because of ligand exchange.

In the K_2ReCl_6–K_2ReBr_6 system of this in-

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vestigation the Re—*X* complexes have weak covalent bonds (Schwochau, 1967; Bell, Rössler, Stöcklin & Upadhyay, 1972) which are quite stable in aqueous solution (Schwochau, 1965) but unstable at high temperature because of the decreasing covalency. Thus, mixed-ligand complexes are formed in the high-temperature solid solution. The quenched samples can be dissolved in aqueous solution and the mixed-ligand complexes separated by electrophoresis and quantitatively determined by activation analysis.

Experimental procedure

Mixtures of recrystallized K_2ReCl_6 (Heraeus, Hanau), K_2ReBr_6 and reagent-grade KCl and KBr were thoroughly ground under acetone and sealed in fused silica tubes at 10^{-2} torr. The samples were equilibrated in vertical tube furnaces where the temperature could be maintained within ±3 °C. After equilibration the samples were rapidly quenched to room temperature and analysed by microscopy and X-ray diffraction. Small amounts of one phase in a mixture could be detected by the film technique with a long exposure time. Intensities for structure factor calculations were obtained by step scanning with a Siemens powder diffractometer.

The infrared spectra were recorded with the Beckman FIR Fourier spectrophotometer FS-720 between 40 and 380 cm^{-1}. The powder samples were finely divided in Nujol on polyethylene.

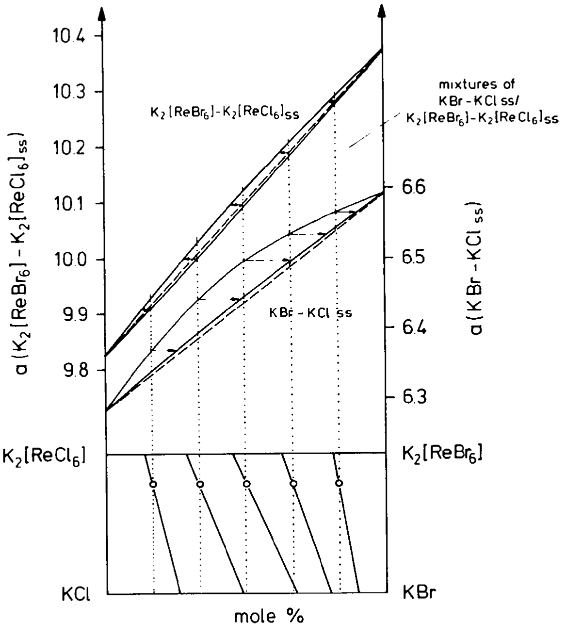

Fig. 1. Lattice constants of K_2ReCl_6–K_2ReBr_6 ss and KCl–KBr ss, and conjugation lines between coexisting phases as determined by X-ray diffraction.

For electrophoretic separation the samples were dissolved in 0·4 *M* H_2SO_4 with 0·004 *M* lactic acid at a concentration of 1 g l^{-1}. About 20 μl of this solution were used for cellogel electrophoresis (Rössler, Otterbach & Stöcklin, 1972). At 600 V and about 20 μA the mixed-ligand complexes could be separated in a length of about 10 cm within 30 min at 10–15 °C. The different spots could be made visible with 0·1*N* $AgNO_3$. They were cut out and the Re content of each was quantitatively analysed after neutron activation with a dose of $D_{n_{th}} = 4{\cdot}6 \times 10^{15}$ cm^{-2} by γ-spectrometric determination of the ^{186}Re 0·14 MeV line with a well-type Ge(Li) semiconductor detector.

Results

Phase relations

Mixtures of K_2ReCl_6 and K_2ReBr_6 reacted to give a complete solid solution at 420 °C within 100 h. At 370 °C there was only an incomplete reaction after this duration. A solid solution obtained at higher temperatures remained unchanged on annealing at 370 °C. Thus equilibrium cannot be obtained below about 420 °C within 100 h by solid-state reaction. At higher temperatures mixtures of K_2ReCl_6, K_2ReBr_6, KCl and KBr react within a shorter time. K_2ReCl_6 and K_2ReBr_6 in separate tubes connected only *via* the gas phase yielded the same reaction products at 420 °C. Obviously, the samples are mainly equilibrated by the gas phase.

K_2ReCl_6 and K_2ReBr_6 melt at 730 and 715 °C respectively, *i.e.* somewhat below the melting points of KCl (770 °C) and KBr (740 °C) (Bellanca, 1939). The liquid could not be quenched but crystallized to K_2ReCl_6–K_2ReBr_6 ss. Only very small amounts of KCl and KBr besides Cl_2 and Br_2 in the gas phase could be determined as decomposition products. $ReCl_3$ and $ReBr_3$ which are stable at high temperature could not be detected by X-ray diffraction. There is no liquid below

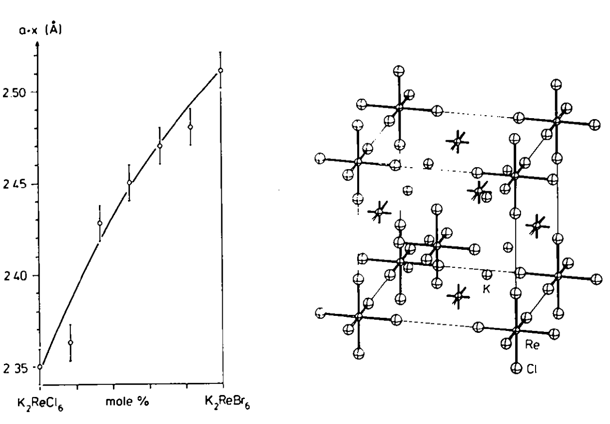

Fig. 2. Crystal structure of K_2ReCl_6 and K_2ReBr_6, and variation of the average Re—*X* bond distance with the composition of the solid solution.

715 °C within the system K_2ReCl_6–K_2ReBr_6–KCl–KBr. At temperatures slightly above the melting point of K_2ReCl_6–K_2ReBr_6 ss, most of the heavy liquid had separated below the KCl–KBr ss within 3 d.

Structural and bonding properties of K_2ReCl_6–K_2ReBr_6 *ss*

The lattice constants of KCl–KBr ss (Bellanca, 1939) and K_2ReCl_6–K_2ReBr_6 ss show a small positive deviation from Vegard's rule (Fig. 1). A non-stoichiometric solid solution could not be obtained in both phases within the limit of detection (2 wt%). Also the lattice constants remained unchanged when small amounts of the coexisting phase were present.

KCl–KBr and K_2ReCl_6–K_2ReBr_6 solid solutions with an equal ratio of Cl/Br in the starting mixture exchanged some halogen during equilibration, thus increasing the Cl content of the hexahalocomplexes as determined by X-ray diffraction (Fig. 1). The X-ray diagrams of K_2ReCl_6–K_2ReBr_6 ss had no additional reflexions and it was assumed that the cubic unit cell of the K_2PtCl_6 structure was maintained in the solid solution. The average Re–X length increases continuously from 2·35 Å in K_2ReCl_6 to 2·51 Å in K_2ReBr_6 (Fig. 2). The positional parameters for pure K_2ReCl_6 and K_2ReBr_6 (x = 0·239 and 0·242 respectively) are in good agreement with the data of previous investigations (Aminoff, 1936; Templeton & Dauben, 1957). Grundy & Brown (1970) reported $x = 0{\cdot}2391$ for both compounds, with a slightly shorter Re–Br distance of 2·48 Å.

The FIR spectra of K_2ReCl_6–K_2ReBr_6 ss contained only single, unsplit absorption bands for the $\nu_3(F_{1u})$ stretching and the $\nu_4(F_{1u})$ bending vibrations of Re–Cl and Re–Br besides lattice vibrations at about 80 cm^{-1} (O'Leary & Wheeler, 1970) (Table 1). With increasing Br content, ν(Re–Cl) decreased quite remarkably, whereas ν(Re–Br) and δ(Re–Cl) showed only a small shift and δ(Re–Br) remained unchanged within the limit of detection (±1 cm^{-1}). These results can be explained by an approximate 10% decrease of the valence force constant of K_2ReCl_6 (1·68 mdyn Å^{-1}) and about a 2% increase of the K_2ReBr_6 valence force constant (1·42 mdyn Å^{-1}) (Schwochau & Krasser, 1969) on changing the Re–Cl and Re–Br length in K_2ReCl_6–K_2ReBr_6 ss.

Table 1. *Far infrared absorption maxima of* K_2ReCl_6–K_2ReBr_6 *ss after annealing for* 3 h *at* 520 °C

Composition of $K_2[ReBr_6]\cdot K_2[ReCl_6]_{ss}$ mole %		Re–X bond lengths, Å	$\nu_4(F_{1u})$, cm^{-1}		$\nu_3(F_{1u})$, cm^{-1}	
			δ(Re–Br)	δ(Re–Cl)	ν(Re–Br)	ν(Re–Cl)
0	100	2.35	–	179	–	329
17	83	2.36	–	176	231	323
33	67	2.43	–	174	230	321
50	50	2.45	–	–	228	319
67	33	2.47	126	–	228	318
83	17	2.48	126	–	228	315
100	0	2.51	126	–	228	–

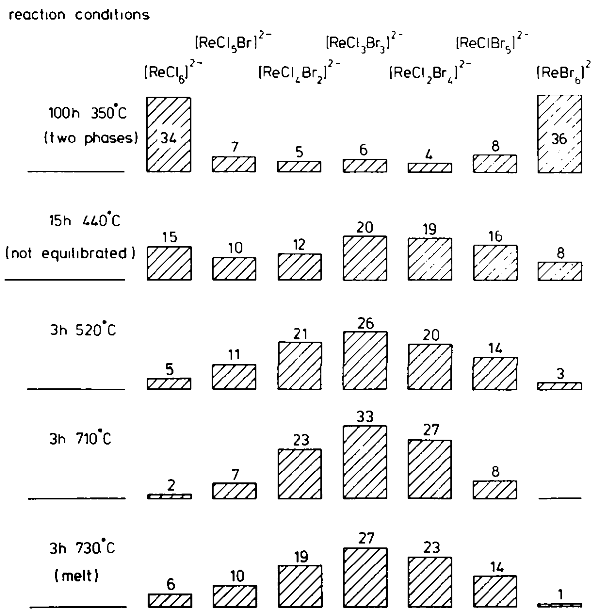

Fig. 3. Yields (%) of mixed-ligand complexes for different reaction conditions from a K_2ReCl_6/K_2ReBr_6 1 : 1 mixture.

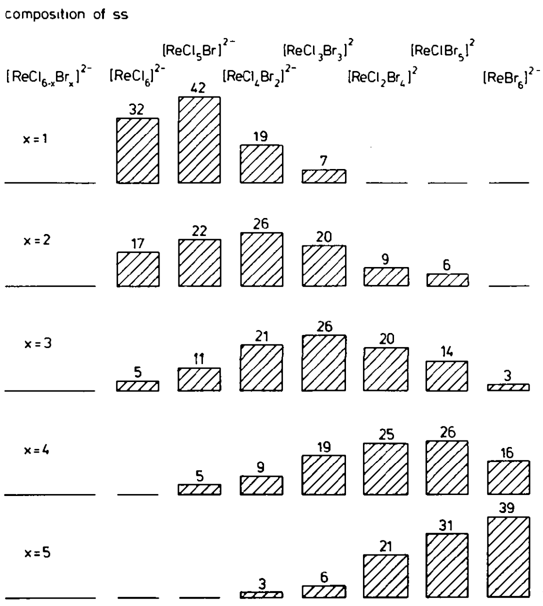

Fig. 4. Yields (%) of mixed-ligand complexes at different compositions of K_2ReCl_6–K_2ReBr_6 ss as obtained at 520 °C.

Distribution of the mixed-ligand complexes

In accordance with the X-ray measurements, the results of the electrophoretic separation showed incomplete reaction for the samples annealed for 100 h at 350°C or 15 h at 440°C respectively (Fig. 3). At higher temperatures the distribution of the mixed-ligand complexes in the 1:1 solid solution was very similar, even in a sample obtained from the liquid.

The concentration variation of the mixed-ligand complexes with the composition of K_2ReCl_6–K_2ReBr_6 ss is shown in Fig. 4. The unsubstituted and monosubstituted complexes usually have a relatively high concentration because of the overall stoichiometry of the sample. The deviations from the original Cl and Br content must be equal on both sides of the major constituent, thus leading to a symmetrical distribution only for the 1:1 solid solution.

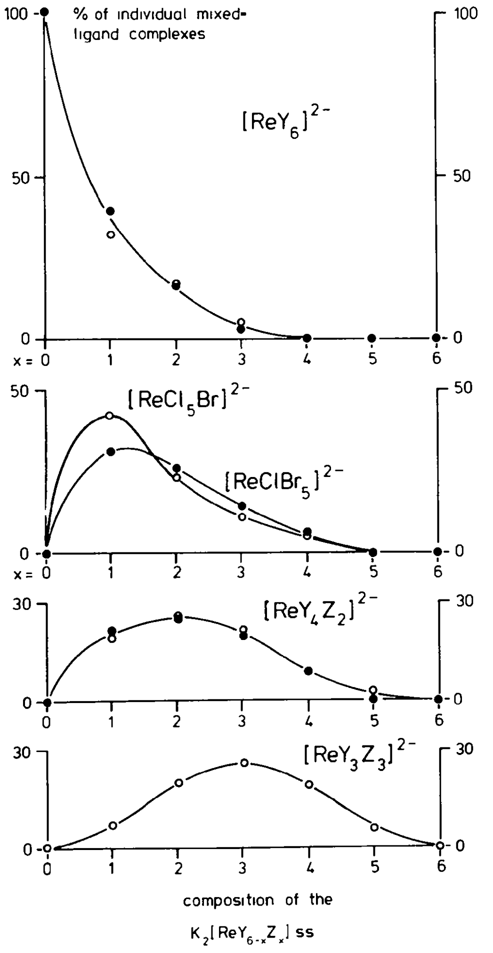

Fig. 5. Comparison of the mixed-ligand yields (%) for substitution by Cl and Br at different compositions of the solid solution.

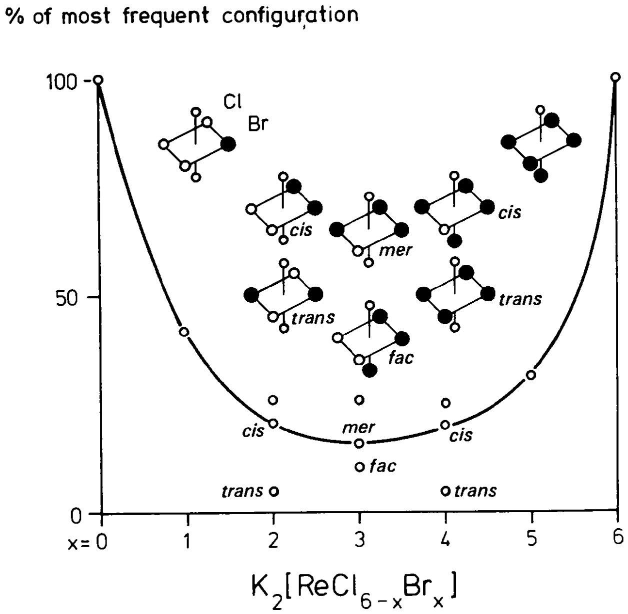

Fig. 6. Yields (%) of the most frequent mixed-ligand complexes at different compositions of K_2ReCl_6–K_2ReBr_6 ss (a statistical distribution was assumed for the stereoisomers; for the composition $x = 5$ the $[ReBr_6]^{2-}$ complex slightly exceeds the $[ReClBr_5]^{2-}$ compound).

Specific differences between Cl and Br substitution can be evaluated by comparison of the concentration of the mixed-ligand complexes as a function of the composition of the crystal (Fig. 5). No differences could be detected for the unsubstituted complexes and for $[ReCl_4Br_2]$ compared with $[ReCl_2Br_4]$ within the limit of error (±2%). For $[ReCl_3Br_3]$ a symmetric distribution was obtained. The concentration maximum of the $[ReCl_5Br]$ complex was found to be considerably higher than that of $[ReClBr_5]$.

The short-range order within the solid solution might be expressed in terms of the concentration of the mixed-ligand complexes. The content of the major component decreases rapidly to a minimum of about 16% at the 1:1 composition (Fig. 6). For the 2:4 and 3:3 complexes different stereoisomers must also be considered which could not be separated by electrophoresis under the conditions applied. For a statistical distribution, the *cis* and *trans* isomers would be formed in a 4:1 ratio, and the meridial and facial isomers in a 3:2 ratio.

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References

AMINOFF, B. (1936). *Z. Kristallogr.* **94A**, 246–248.

BELL, R., RÖSSLER, K., STÖCKLIN, G. & UPADHYAY, S. R. (1972). *J. Inorg. Nucl. Chem.* **34**, 461–475.

BELLANCA, A. (1939). *Period. Miner. (Roma)*, **10**, 9–20.

GRUNDY, H. D. & BROWN, I. D. (1970). *Canad. J. Chem.* **48**, 1151–1154.
JØRGENSEN, C. K., PREETZ, W. & HOMBORG, H. (1971). *Inorg. Chim. Acta*, **5**, 223–230.
KRUSE, F. H. (1961). *Acta Cryst.* **14**, 1035.
MÜLLER, H. (1963). *Z. anorg. allgem. Chem.* **321**, 124–137.
O'LEARY, G. P. & WHEELER, R. G. (1970). *Phys. Rev.* **B1**, 4409–4439.
RÖSSLER, K., OTTERBACH, J. & STÖCKLIN, G. (1972). *J. Phys. Chem.* **76**, 2499–2506.
SCHWOCHAU, K. (1965). *Z. Naturforsch.* **20a**, 1286–1289.
SCHWOCHAU, K. (1967). Report Jül-465-RC, Institut für Chemie der KFA-Jülich.
SCHWOCHAU, K. & KRASSER, W. (1969). *Z. Naturforsch.* **24a**, 403–407.
TEMPLETON, D. H. & DAUBEN, C. H. (1957). *J. Amer. Chem. Soc.* **73**, 4422–4493.
WASASTJERNA, J. A. (1946). *Soc. Sci. Fenn. Commentat. Phys. Math.* **13**, 1–24.

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The Crystal and Molecular Structure of 4β,5β-Epoxycholestan-3-one

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The title steroid is orthorhombic, with $a = 25{\cdot}08\,(1)$, $b = 10{\cdot}866\,(5)$, $c = 9{\cdot}118\,(5)$ Å, $Z = 4$, space group $P2_12_12_1$. The structure was determined from diffractometer data and refined by full-matrix least squares to a final R of 0·079 for 945 independent reflexions. Ring A is *cis*-fused to ring B whilst the remaining rings are *trans*-fused, the side chain being in an extended configuration.

Introduction

4β,5β-Epoxycholestan-3-one was prepared from cholestan-4-en-3-one (as an intermediate in the synthesis of 4-hydroxycholest-4-en-3-one, which is being studied as a metal-complexing agent) by reaction with alkaline hydrogen peroxide (Henbest & Jackson, 1967). Only the 4β,5β-epoxide was formed, in agreement with Henbest & Jackson who reported that Δ^4-3-keto-steroids not containing polar substituents yield exclusively the corresponding β-epoxide, whereas the presence of polar substituents at positions as remote from the site of reaction as C(17) results in the formation of mixtures containing varying amounts of the corresponding α-epoxides.

Experimental

The compound (m.p. 116–117 °C) was recrystallized from ether–methanol. Microanalysis yielded the following results:

	C	H
Found	80·70%	11·30%
Calculated for $C_{27}H_{44}O_2$	80·87	11·07.

The crystals were colourless needles elongated along **b**.

Preliminary photographs (Cu $K\alpha$ radiation, $\lambda = 1{\cdot}542$ Å) showed systematic absences $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$ and $00l$, $l = 2n + 1$, indicating space group $P2_12_12_1$. Crystal data are listed in Table 1.

The cell parameters of a crystal (0·68 × 0·16 × 0·12 mm) were obtained by least squares from the settings of 25 reflexions measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å, graphite-monochromated). The intensities of 1944 reflexions in the range $3° < \theta < 23°$ were recorded by the ω–2θ scan technique (scan width 0·9° θ, scan speed 0·03° $\theta\ \mathrm{s}^{-1}$). The background was counted on both sides of the peak for one half of the peak scan time. The intensities of three standard reflexions measured every hour remained constant to within 1·8% of their mean values. Lorentz–polarization corrections were applied. No absorption correction was made. With the criterion $I(\mathrm{rel.}) > 2\sigma I(\mathrm{rel.})$ for an observed reflexion, 999 were omitted leaving 945 unique reflexions for the analysis.

Table 1. *Crystal data*

Molecular formula: $C_{27}O_2H_{44}$
Space group $P2_12_12_1$
$a = 25{\cdot}08\,(1)$ Å
$b = 10{\cdot}866\,(5)$
$c = 9{\cdot}118\,(5)$
$V = 2484{\cdot}53$ Å^3
$M_r = 400$
$D_m = 1{\cdot}09\ \mathrm{g\ cm^{-3}}$
$D_c = 1{\cdot}08$ for $Z = 4$
$\mu = 0{\cdot}34\ \mathrm{cm^{-1}}$
$F(000) = 888$

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