UNICS (Crystallographic Society of Japan, 1967). Fig. 2 was drawn using *ORTEP* (Johnson, 1965).

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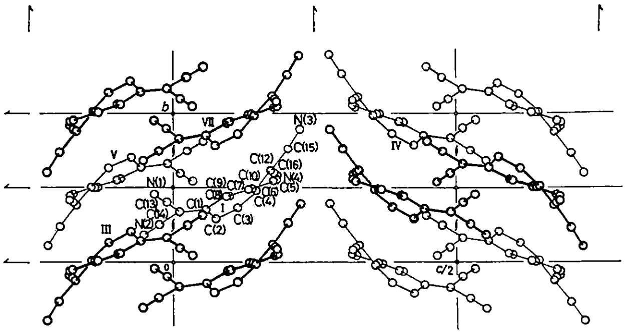

Fig. 6. Projection of the structure along the *a* axis.

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The Crystal Structures of Dichlorobis-(2,3-dimethylpyridine)copper(II) and Dibromobis-(2,3-dimethylpyridine)copper(II)

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Dichlorobis-(2,3-dimethylpyridine)copper(II) [=CuL_2Cl_2] and dibromobis-(2,3-dimethylpyridine)copper(II) [=CuL_2Br_2] are isotypic with the following monoclinic unit-cell dimensions: CuL_2Cl_2: a= 7·461 (4), b=14·80 (1), c=7·879 (6) Å, β=110·11 (5)°; CuL_2Br_2: a=7·566 (5), b=15·33 (2), c= 7·899 (6) Å, β=109·72 (6)°. The space group is $P2_1/c$. The structure determination from Patterson and Fourier syntheses was followed by a full-matrix least-squares refinement including anisotropic thermal parameters. For CuL_2Cl_2 the final R value for 961 observed Weissenberg reflexions was 6·8%, whereas for 831 observed Weissenberg reflexions of CuL_2Br_2 a R value of 7·6% was obtained. The structures consist of isolated CuL_2Cl_2 (CuL_2Br_2) units with exactly planar, *trans* square coordination of the copper atom. The Cu-Cl distance is 2·25 Å, the Cu-Br distance is 2·39 Å and the Cu–N distance is 1·98 Å. The fact that there are no further ligands in the neighbourhood of the copper atom which would lead to its common distorted octahedral coordination is attributed to the steric influence of the methyl groups in the α position to the nitrogen atoms.

Introduction

Ludwig & Gasser (1969) reported on the preparation and on spectroscopical investigations on copper(II) complexes of the general formula CuL_2X_2 and CuL_4X_2 where L stands for a unidendate substituted pyridine or piperidine base and X for a halide.

For complexes containing unsubstituted pyridine they found a microsymmetry of D_{2h} with a distorted octahedron consisting of two pyridine, two equatorial halides and two axial halides as ligands, in accordance with the crystal structure determination of dichlorodipyridinecopper(II) (Dunitz, 1957). For α-, or α,β- or α,α'-substituted ligands the electronic spectra pointed to various coordinations from planar to distorted tetrahedral. The present paper reports on the crystal structure of dichlorobis-(2,3-dimethylpyridine)copper(II) and dibromobis-(2,3-dimethylpyridine)copper(II), two complexes for which Ludwig & Gasser determined a microsymmetry of D_{2h} and a planar coordination around the copper ion.

Experimental

Samples of dichlorobis-(2,3-dimethylpyridine)copper(II)[$=CuL_2Cl_2$] and dibromobis-(2,3-dimethylpyridine)-(II) [$=CuL_2Br_2$] were recrystallized from methylene chloride. The single crystals obtained were elongated prisms with approximately hexagonal cross section. X-ray powder diagrams for the determination of accurate unit-cell dimensions were taken with a focusing camera of the Guinier–de Wolff type with Cu $K\alpha$ radiation. High purity potassium chloride was used as an internal standard. Multiple-film integrated Weissenberg photographs (layers $hk0$, $hk1$, ..., $hk7$ for CuL_2Cl_2 and layers $hk0$, $hk1$, ..., $hk4$ for CuL_2Br_2) were taken on a Nonius camera with Cu $K\alpha$ radiation (Ni filter). Intensities of the layers $h0l$ and $0kl$ were collected by the multiple exposure technique with Zr-filtered Mo radiation on a Buerger precession camera. The blackening of the films was measured with a Joyce–Loebl mark III CS double-beam microdensitometer. The data from the layers $h0l$ and $0kl$ were used to bring the observed structure factors of the layers $hk0$ to $hk7$ on the same scale.

The intensities were reduced to F_o by applying Lorentz, polarization and absorption factors. The absorption correction was accomplished using the formula proposed by Palm (1964). Structure factor calculations were performed on a IBM/360/40 computer using a program written by Meier & Gramlich (1968). Fourier syntheses (King & Van der Helm, 1963) were calculated on a IBM 1620 system. Full-matrix least-squares refinement was executed on a CDC 6500

Table 1. *Final observed and calculated structure amplitudes for dichlorobis-*(2,3-*dimethylpyridine*)*copper*(II)

The columns are h, k, F_o, $|F_c|$.

[illegible]

Table 2. *Final observed and calculated structure amplitudes for dibromobis-*(2,3-*dimethylpyridine*) *copper*(II)

The columns are h, k, F_o, $|F_c|$.

[illegible]

electronic data processing system using the program *XFLS* by Busing, Martin & Levy (1967).

Crystal data

Dichlorobis-(2,3-dimethylpyridine)copper(II) and dibromobis-(2,3-dimethylpyridine)copper(II) are monoclinic with the following unit-cell dimensions (refined by least-squares calculations):

CuL_2Cl_2	CuL_2Br_2
$a=7{\cdot}461(4)$ Å	$a=7{\cdot}566(5)$ Å
$b=14{\cdot}80(1)$	$b=15{\cdot}33(2)$
$c=7{\cdot}879(6)$	$c=7{\cdot}899(6)$
$\beta=110{\cdot}11(5)^\circ$	$\beta=109{\cdot}72(6)^\circ$
$V=817(1)$ Å^3	$V=862(1)$ Å^3
Z = 2 formula units per cell	Z = 2 formula units per cell
$d_x=1{\cdot}423$ g.cm^{-3}	$d_x=1{\cdot}706$ g.cm^{-3}

Temperature 22 °C
(values in parentheses are standard deviations).

The crystals used for data collection had the following dimensions:

CuL_2Cl_2 0·24 × 0·25 × 1·00 mm
(along **a**, **b**, **c** respectively)
CuL_2Br_2 0·24 × 0·22 × 0·80 mm
(along **a**, **b**, **c** respectively)

The linear absorption coefficents for copper radiation are:

CuL_2Cl_2: 48·24 cm^{-1}
CuL_2Br_2: 43·74 cm^{-1}

The space group, as determined from Weissenberg and precession photographs is $P2_1/c$.

Structure solving and refinement

Initially a three-dimensional Patterson synthesis was computed with the *hk*0, *hk*1, ..., *hk*4 reflexions of CuL_2Cl_2. It revealed the positional parameters of the copper and chlorine atoms. By several successive difference Fourier syntheses the positions of the nitrogen and the seven carbon atoms were determined. The R value at this point was 18·5%. Further calculations were carried out with the least-squares refinement program *XFLS* using relativistic Hartree–Fock X-ray scattering factors (Doyle & Turner, 1968) corrected for anomalous dispersion with the values for $\Delta f'$ and $\Delta f''$given by Cromer (1965). During the refinement it turned out that the observed intensities were affected by secondary extinction. The correction for this effect was accomplished with a formula given by Stout & Jensen (1968). After variation of 27 positional, 10 isotropic temperature factors, and 8 scale factors the R value* for the 961 observed Weissenberg reflexions of the layers *hk*0, *hk*1, ..., *hk*7 decreased to 9·9% and the weighted R value R'* to 10·3%. After introduction of anisotropic temperature factors and computed positions of the three hydrogen atoms of the pyridine ring the R value was reduced to 6·8% and R' to 7·2%. In the last cycle we varied 36 positional

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* $R=\sum|F_o-|F_c||/\sum F_o$
$R'=\sum(F_o-|F_c|)^2/\sum F_o^2$

Table 3. *Positional and thermal parameters for dichlorobis-*(2,3-*dimethylpyridine*)*copper*(II)

Positional parameters

	x	y	z
Cu	0·0000	0·5000	0·5000
Cl	0·0384 (3)	0·4018 (1)	0·2965 (3)
N	0·2396 (8)	0·4550 (4)	0·6804 (7)
C(1)	0·2438 (10)	0·3888 (5)	0·8011 (9)
C(2)	0·4128 (12)	0·3584 (5)	0·9213 (10)
C(3)	0·5804 (12)	0·3954 (6)	0·9182 (12)
C(4)	0·5782 (12)	0·4627 (6)	0·7988 (12)
C(5)	0·4029 (11)	0·4912 (6)	0·6859 (11)
C(6)	0·0500 (12)	0·3520 (6)	0·7930 (13)
C(7)	0·4138 (15)	0·2838 (6)	0·0566 (14)
H(1)	0·736 (13)	0·376 (6)	0·998 (13)
H(2)	0·686 (13)	0·503 (6)	0·785 (12)
H(3)	0·412 (13)	0·551 (6)	0·587 (13)

Mean-square amplitudes of vibration (Å^2 × 10^{-3})

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	39 (1)	40 (1)	37 (1)	2 (1)	7 (1)	2 (1)
Cl	64 (1)	63 (1)	52 (1)	9 (2)	6 (2)	−12 (2)
N	33 (3)	44 (3)	35 (3)	4 (5)	10 (5)	0 (5)
C(1)	49 (4)	40 (4)	33 (4)	4 (6)	11 (6)	4 (6)
C(2)	58 (4)	51 (4)	35 (4)	6 (6)	3 (6)	2 (6)
C(3)	49 (4)	61 (4)	50 (4)	4 (6)	3 (6)	−3 (6)
C(4)	37 (4)	69 (4)	67 (4)	−4 (6)	17 (6)	−2 (6)
C(5)	45 (4)	57 (4)	51 (4)	0 (6)	14 (6)	−4 (6)
C(6)	56 (5)	63 (5)	75 (5)	−9 (7)	22 (7)	18 (7)
C(7)	103 (5)	60 (5)	71 (5)	21 (7)	15 (7)	21 (7)

H(1), H(2), H(3) were given isotropic, not refined thermal parameters $B=4{\cdot}0$ Å^2.

and 60 thermal parameters. The function minimized was $\sum|F_c-F_o|^2$. The reflexions were given unit weights. The final observed and calculated structure amplitudes for CuL_2Cl_2 are listed in Table 1.

The structure of the isotropic compound CuL_2Br_2 was solved as follows. The positional parameters and the isotropic temperature factors of CuL_2Cl_2 were used as starting values for the least-squares refinement. After several cycles of refinement the R values for the 831 observed Weissenberg reflexions of CuL_2Br_2 were $R = 10{\cdot}5\%$ and $R' = 10{\cdot}2\%$. After introduction of anisotropic temperature factors and variation of 87 positional and thermal parameters R decreased to 7·6% and R' to 7·4%. No hydrogen positions were introduced. The final observed and calculated structure amplitudes for CuL_2Br_2 are given in Table 2. The positional and thermal parameters for CuL_2Cl_2 and CuL_2Br_2 are listed in Tables 3 and 4.

Description of the structure

The structures of dichlorobis-(2,3-dimethylpyridine)-copper(II) and dibromobis-(2,3-dimethylpyridine)copper(II) are isotropic and can be characterized as follows. (The description is restricted to CuL_2Cl_2 but the same is valid for CuL_2Br_2.) The structure is built up of isolated CuL_2Cl_2 units and the copper atoms are coordinated by two chlorine and two nitrogen atoms. As the copper atoms are situated on a centre of inversion, the coordination has to be exactly planar, *trans* square. A projection of one CuL_2Cl_2 unit along **b** is given in Fig. 1. The interatomic distances and bond

Table 4. *Positional and thermal parameters for dibromobis*-(2,3-*dimethylpyridine*)*copper*(II)

Positional parameters

	x	y	z
Cu	0·0000	0·5000	0·5000
Br	0·0353 (2)	0·3971 (1)	0·2859 (2)
N	0·2328 (12)	0·4558 (6)	0·6812 (14)
C(1)	0·2374 (16)	0·3902 (8)	0·7892 (18)
C(2)	0·3993 (18)	0·3578 (8)	0·9175 (22)
C(3)	0·5708 (18)	0·3964 (11)	0·9080 (24)
C(4)	0·5655 (18)	0·4623 (10)	0·7979 (25)
C(5)	0·3970 (17)	0·4929 (8)	0·6824 (20)
C(6)	0·0506 (19)	0·3535 (10)	0·7822 (24)
C(7)	0·4020 (23)	0·2843 (10)	0·0482 (22)

Mean-square amplitudes of vibration ($Å^2 \times 10^{-3}$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	44 (1)	43 (1)	41 (1)	2 (2)	10 (2)	0 (2)
Br	72 (1)	72 (1)	63 (1)	10 (2)	14 (2)	−12 (2)
N	52 (5)	44 (5)	34 (6)	−1 (8)	10 (8)	−2 (8)
C(1)	59 (6)	48 (5)	26 (6)	4 (10)	22 (10)	2 (10)
C(2)	59 (6)	46 (5)	69 (6)	4 (10)	14 (10)	0 (10)
C(3)	51 (6)	77 (6)	96 (6)	3 (10)	12 (10)	−4 (10)
C(4)	47 (6)	76 (6)	103 (6)	1 (10)	11 (10)	−19 (10)
C(5)	53 (6)	68 (6)	64 (6)	−12 (10)	16 (10)	−16 (10)
C(6)	55 (7)	81 (7)	100 (7)	6 (11)	20 (11)	8 (11)
C(7)	115 (7)	80 (7)	53 (7)	17 (11)	0 (11)	17 (11)

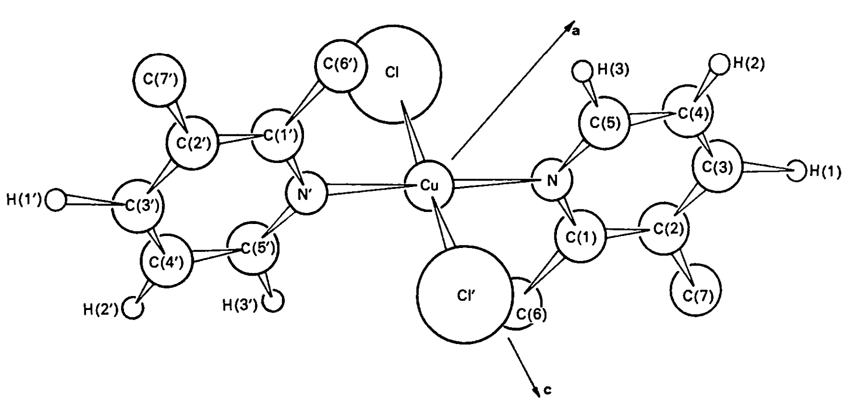

Fig. 1. One CuL_2Cl_2 unit of the structure of dichlorobis-(2,3-dimethylpyridine)copper(II) projected along **b**.

angles for CuL_2Cl_2 and CuL_2Br_2 are given in Tables 5 and 6.

Table 5. *Interatomic distances and bond angles for dichlorobis-*(2,3-*dimethylpyridine*)*copper*(II)

(*a*) Coordination around Cu

Cu-Cl	2·254 (2) Å
Cu-N	1·977 (6)
Cl -N	2·983 (6)
Cl -N′	3·014 (6)
N—Cu-Cl	89·4 (3)°

Symmetry code ′ = $-x,\ -y,\ -z$

(*b*) Dimethylpyridine ring

N—C(1)	1·357 (9) Å
N—C(5)	1·317 (11)
C(1)-C(2)	1·366 (10)
C(1)-C(6)	1·526 (11)
C(2)-C(3)	1·373 (12)
C(2)-C(7)	1·533 (13)
C(3)-C(4)	1·365 (13)
C(3)-H(1)	1·15 (10)
C(4)-C(5)	1·371 (13)
C(4)-H(2)	1·03 (10)
C(5)-H(3)	1·19 (10
C(5)-N—C(1)	118 (1)°
N—C(1)-C(6)	116 (1)
N—C(1)-C(2)	121 (1)
C(1)-C(2)-C(3)	119 (1)
C(2)-C(3)-C(4)	120 (1)
C(3)-C(4)-C(5)	117 (1)
C(4)-C(5)-N	124 (1)
C(6)-C(1)-C(2)	123 (1)
C(1)-C(2)-C(7)	120 (1)
C(7)-C(2)-C(3)	121 (1)

Table 6. *Interatomic distances and bond angles for dibromobis-*(2,3-*dimethylpyridine*)*copper*(II)

(*a*) Coordination around Cu

Cu-Br	2·392 (2) Å
Cu-N	1·976 (9)
Br -N	3·105 (9)
Br -N′	3·101 (9)
N—Cu-Br	90·1 (4)°

Symmetry code ′ = $-x,\ -y,\ -z$

Table 6 (*cont.*)

(*b*) Dimethylpyridine ring

N—C(1)	1·311 (15) Å
N—C(5)	1·363 (17)
C(1)-C(2)	1·391 (19)
C(1)-C(6)	1·504 (21)
C(2)-C(3)	1·450 (23)
C(2)-C(7)	1·524 (22)
C(3)-C(4)	1·324 (23)
C(4)-C(5)	1·376 (21)
C(5)-N—C(1)	119 (2)°
N—C(1)-C(6)	116 (2)
N—C(1)-C(2)	125 (2)
C(1)-C(2)-C(3)	114 (3)
C(2)-C(3)-C(4)	121 (3)
C(3)-C(4)-C(5)	121 (3)
C(4)-C(5)-N	120 (2)
C(6)-C(1)-C(2)	119 (3)
C(1)-C(2)-C(7)	124 (3)
C(7)-C(2)-C(3)	122 (3)

Discussion of the structure

In many cupric compounds the square planar coordination of copper is completed to a distorted octahedral one. This may be achieved by stacking the motive consisting of Cu and its four ligands in such a way that copper is coordinated by two further ligands at a considerably longer distance. Examples for this characteristic behaviour are the structures of $CuCl_2\cdot 2H_2O$ (Harker, 1936; Peterson & Levy, 1957), dichlorodipyridinecopper(II) (Dunitz, 1957), $CuCl_2$ (Wells, 1947), $CuBr_2$ (Helmholz, 1947).

In the structures of CuL_2Cl_2 and CuL_2Br_2 such a coordination is not possible because the methyl groups in the α-position of the pyridine rings prevent chlorine or nitrogen atoms of adjacent CuL_2Cl_2 units from coming close to the copper atom. As can be seen in Fig. 1 the planes of the dimethylpyridine rings are approximately at right angles to the plane containing the copper, the two chlorine and the nitrogen atoms. In this arrangement the interference of the methyl groups with the chlorine atoms is minimized but the methyl groups C(6) and C(6′) are now almost in the position where the farther ligands in a distorted octahedral coordination would be expected. The Cu–C(6) distance is 2·95 Å, a value comparable to the longer

Table 7. *Interatomic distances of various cupric complexes with distorted octahedral and square planar coordination of the copper atom*

Compound	Cu(II)-X	Cu(II)-N	Reference
Distorted octahedron			
$CuCl_2$	2·30/2·95	—	Wells (1947)
$CuBr_2$	2·40/3·18	—	Helmholz (1947)
$CuCl_2.2H_2O$	2·28/2·95	—	Harker (1936); Peterson & Levy (1957)
$CuCl_2$(pyridine)$_2$	2·28/3·05	2·02	Dunitz (1957)
Cu(II) $(NH_3)_4[Cu(I)Cl_2]_2H_2O$	—	2·03	Baglio & Vaughan (1970)
Square planar			
Cu(II) $(NH_3)_4[Cu(I)Br_2]_2$	—	2·00	Baglio & Vaughan (1970)
CuL_2Cl_2	2·25	1·98	Present paper
CuL_2Br_2	2·39	1·98	Present paper

Cu–Cl distance of 3·05 Å in dichlorodipyridinecopper(II) (Dunitz, 1957).

The crystal structure determination thus agrees well with the results of the spectroscopic investigations cited before. The Cu–Cl, Cu–Br and Cu–N bond lengths are all slightly shorter than the values reported for distorted octahedral coordination (see Table 7). This may be due to stronger Cu–Cl, Cu–Br and Cu–N bonds in the square planar coordination. The carbon-to-carbon and carbon-to-nitrogen bond distances found for the dimethylpyridine ring agree well with previous reported values (Dunitz, 1957; *International Tables for X-ray Crystallography*, 1962).

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The Crystal Chemistry of Zirconium Sulphates. IX. The Structure of $K_2[Zr(SO_4)_3].2H_2O$

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The structure of $K_2[Zr(SO_4)_3].2H_2O$ has been determined by single-crystal X-ray analysis and refined by least squares. The crystals are monoclinic, space group $P2_1/c$ and have unit-cell dimensions $a=7{\cdot}40$, $b=13{\cdot}96$, $c=12{\cdot}79$ Å, $\beta=96{\cdot}6°$. The structure consists of dimeric units of composition $[Zr_2(SO_4)_6(H_2O)_4]^{4-}$ which are held together by the potassium ions. Two of the sulphate groups form a double bridge between the pairs of zirconium atoms and two sulphate groups are doubly bonded to each of the zirconium atoms which are eight-coordinated to oxygen atoms. All the sulphate groups have two terminal oxygen atoms. Two water molecules are also coordinated to each of the zirconium atoms. It is seen that the structure of $K_2[Zr(SO_4)_3].2H_2O$ is closely related to those of $Zr(SO_4)_2.7H_2O$ and α- and β-$Zr(SO_4)_2.5H_2O$.

Introduction

The transformations among the neutral hydrates of $Zr(SO_4)_2$ and α-$Zr(SO_4)_2$ have previously been discussed (Bear & Mumme, 1970). The structures of these compounds showed striking similarities in their general three-dimensional arrangements of zirconium and sulphur atoms. The similarity of arrangement was found to prevail even though the hepta- and α- and β-pentahydrates contained isolated dimeric units, the tetra- and γ- and α-monohydrates were hydrogen bonded layer-type structures and α-$Zr(SO_4)_2$ a three-dimensional network of sulphate bridged zirconia polyhedra.

We are now examining the effect of introducing into these structures large ions such as the alkali metals and have previously determined the structure of the double salt $Na_2[Zr(SO_4)_3].3H_2O$ (Bear & Mumme, 1971). The present paper describes the crystal structure of the salt $K_2[Zr(SO_4)_3].2H_2O$ and relates its structure to that of $Na_2[Zr(SO_4)_3].3H_2O$ and the structures of the compounds already determined in our investigations of the $Zr(SO_4)_2$-H_2O system.

Experimental

Single crystals of $K_2[Zr(SO_4)_3].2H_2O$ were grown from solution following the method described by Sokol, Atana & Zaitser (1967). However, a single phase