Binuclear Chromium(III) Complexes with Squarate and Bis(2-pyridylmethyl)amine. Crystal Structure and Magnetic Characterization of Di-μ-hydroxobis[{bis(2-pyridylmethyl)-amine}squaratochromium(III)] Hydrate

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$[(bispicam)Cr(OH)_2(C_4O_4)Cr(bispicam)]Br_2 \cdot 2\ H_2O$ and $[(H_2O)(bispicam)Cr(OH)_2 Cr(bispicam)(C_4O_4)]Cl_2 \cdot 4\ H_2O$ could be separated from a reaction mixture containing chromium(II) squarate and bis(2-pyridylmethyl)amine (bispicam). The reaction between chromium(II) sulfate and bispicam in the presence of barium hydroxide leads to $[(H_2O)(bispicam)Cr(OH)]_2^{4+}$, which was isolated as a chloride salt. The acid form of this salt reacted further with squaric acid to give $[(C_4O_4)(bispicam)Cr(OH)]_2 \cdot 8\ H_2O$ (**1**).

The structure of **1** was determined from X-ray diffraction data. The complex crystallizes in the monoclinic space group $P\ 2_1/n$ with $a = 10.528(1)$, $b = 13.166(1)$, $c = 14.800(1)$ Å, $\beta = 104.81(1)°$ and $Z = 2$. The dihydroxo-bridged complex has a centre of inversion, and the tridentate amine is in *meridional* coordination.

The magnetic susceptibilities of the compounds were interpreted in terms of antiferromagnetic two-centre exchange interaction. For **1** we found a triplet energy $J = 10.53(5)\ cm^{-1}$. This value is in very good agreement with the structural parameters according to the GHP model.

The magnetic properties of chromium(III) in exchange-coupled systems has been an area of recent intense research. Most of the systems studied so far have hydroxo groups as bridging ligands, and amine-like ligands at the remaining coordination sites. In this work we have investigated the rôle of squarate ions in dinuclear di-μ-hydroxochromium(III) complexes with the tridentate amine bis(2-pyridylmethyl)amine (bispicam, Fig. 1). The squarate ion is known to act as a bridging ligand, but in contrast to the oxalate ion it has not yet been seen as a chelate ligand.

In squarates of the general composition $[M(C_4O_4)(H_2O)_2]_\infty$ with M = Mn(II), Fe(II), Co(II) or Ni(II), the oxygen atoms in $C_4O_4^{2-}$ bridge four metal atoms forming a sheet structure.[1] In squarates with the formula $[M(C_4O_4)(H_2O)_4]_\infty$, where M = Zn(II) or the metals mentioned above, and also in $[Ni(C_4O_4)(C_3H_4N_2)_2(H_2O)_2]_\infty$, two opposite oxygen atoms in $C_4O_4^{2-}$ are involved in metal bridging.[2,3] Finally, $\{[Ni(C_4O_4)(C_{10}H_8N_2)_2(H_2O)_2] \cdot 2\ H_2O\}_\infty$ and trivalent metal squarates of the composition $[M(C_4O_4)(OH)(H_2O)_2]_2 \cdot 2\ H_2O$ with M = Al(III), Cr(III) and Fe(III) have two adjacent squarate oxygen atoms involved in metal bridging.

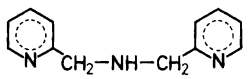

Fig. 1. Bis(2-pyridylmethyl)amine, $C_{12}H_{13}N_3$, bispicam.

We have synthesized three different dinuclear compounds which have two hydroxo groups as bridging ligands as a common feature. An X-ray structure analysis of one of these compounds revealed centrosymmetric complex cations with monodentate squarate ligands and tridentate amines in *meridional* coordination. For a second compound there is chemical evidence for *meridional* amine coordination, and for either a terminal monodentate squarate ligand on one of the chromium atoms or for squarate ions bridging adjacent dinuclear complexes to form infinite chains. A third compound evidently contains the di-μ-hydroxo-μ-squarato complex with the amine in a *facial* configuration.

Experimental

Chemicals, elemental analysis and apparatus. Squaric acid (3,4-dihydroxo-3-cyclobutene-1,2-dione) was purchased from Fluka AG, Buchs, Switzerland. Chromium(II) sulfate pentahydrate was prepared by standard methods. The preparations of chromium(II) squarate dihydrate and of bis(2-pyridylmethyl)-amine trihydrochloride monohydrate, $C_{12}H_{13}N_3 \cdot 3\ HCl \cdot H_2O$, are described elsewhere.[6,7]

The chromium analyses were performed on a Perkin Elmer 403 Atomic Absorption Spectrophotometer. The

microanalytical laboratory of the H. C. Ørsted Institute carried out the carbon, nitrogen, hydrogen and halogen analyses by standard methods.

Absorption spectra were recorded on a Cary Model 14 spectrophotometer. The spectra are characterized by their maxima and minima (ε, λ), where the molar extinction coefficient ε is in units of l mol^{-1} cm^{-1} and λ is nm. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 4.0–300 K at a field strength of 1.3 T. $Hg[Co(NCS)_4]$ was used as calibrant for susceptibility at room temperature. The temperature scale below 77 K was calibrated using a solid solution of 1 mol % hexamminechromium(III) ions in hexamminecobalt(III) iodide. Diamagnetic corrections were made using Pascal constants. The apparatus is described elsewhere.[8,9] The X-ray powder photographs were obtained using a camera of the Hägg–Guinier type with Cu*K*α radiation. Silicon was used as standard.

Preparations. 1. Di-μ-hydroxo-μ-squarato-bis[{bis(2-pyridylmethyl)amine}chromium(III)] bromide dihydrate, $[(C_{12}H_{13}N_3)Cr(OH)_2(C_4O_4)Cr(C_{12}H_{13}N_3)]Br_2 \cdot 2\ H_2O$. Bispicam · 3 HCl · H_2O (3.27 g, 10.0 mmol) was dissolved in water (20 ml). The pH of the solution was adjusted to 7.0 with aqueous sodium hydroxide (2 M, ~12 ml). Chromium (II) squarate dihydrate (2.00 g, 10.0 mmol) was added with stirring, and the reaction started immediately. After 1 h, pH of the solution remained constant (~4.2), and the solution was filtered. The filtrate was transferred to a column of SP-Sephadex C-25 (length 10 cm, diam. 7 cm) and the column was eluted with aqueous sodium sulfate (0.1 M). Several red bands appeared on the column. The eluate containing the first red major band was diluted five times and transferred to a shorter column, where sodium and sulfate ions were eluted with hydrobromic acid (0.1 M). The red compound was subsequently eluted with aqueous lithium bromide (1 M). The dark red crystals that separated from the last eluate were filtered off and washed with ethanol (99 %). Yield: 0.58 g (13.7). Anal. $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)]Br_2 \cdot 2\ H_2O$: Cr, C, N, H, Br. Sometimes the compound crystallized with 5 mol of crystal water. $(\varepsilon, \lambda)_{max}$: (101, 535). $(\varepsilon, \lambda)_{min}$: (32.9, 459). The corresponding perchlorate was obtained when sodium perchlorate (1 g) was added to a concentrated solution of the dark red bromide (0.50 g) in water (6.5 ml). After cooling on ice the crystals were filtered off and washed with a solution of sodium perchlorate (1 M) and with ethanol. Yield: 0.41 g. Anal. $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)](ClO_4)_2 \cdot 5\ H_2O$; Cr, C, N, H, Cl.

2. Aqua{bis(2-pyridylmethyl)amine}chromium(III)-di-μ-hydroxo-{bis(2-pyridylmethyl)amine}squaratochromium(III) chloride tetrahydrate, $[(H_2O)(C_{12}H_{13}N_3)Cr(OH)_2Cr(C_{12}H_{13}N_3)(C_4O_4)]Cl_2 \cdot 4\ H_2O$. The eluate containing the second red band (see prep. 1) was diluted five times and transferred to a shorter column, and sodium and sulfate ions were eluted with 0.1 M hydrochloric acid. The red complex was eluted with 0.4 M hydrochloric acid. The orange-red crystals that separated were washed with ethanol (96 %). Yield: 0.10 g (1.5 %). Anal. $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)(H_2O)]Cl_2 \cdot 4\ H_2O$: Cr, C, N, H, Cl. $(\varepsilon, \lambda)_{max}$: (89.8, 519), $(\varepsilon, \lambda)_{min}$: (32.9, 448).

3. Di-μ-hydroxo-bis[{bis(2-pyridylmethyl)-amine}aquachromium(III)]chloride heptahydrate, $[(H_2O)(C_{12}H_{13}N_3)Cr(OH)_2Cr(H_{12}H_{13}N_3)(H_2O)]Cl_4 \cdot 7\ H_2O$. Bispicam 3 HCl · H_2O (4.90 g, 15.0 mmol) was dissolved in water (45 ml). Barium hydroxide octahydrate (6.31 g, 2.00 mmol) was added followed by crushed chromium(II) sulfate pentahydrate (3.57 g, 15.0 mmol). The mixture was stirred for 20 h. After filtering, the solution was transferred to a Sephadex column (length 20 cm, diam. 7 cm) and eluted with an aqueous phosphate solution (0.5 M Na_2HPO_4–0.05 M NaH_2PO_4) until the first major band (blue) had beenisolated from the other bands (compounds of higher nuclearity). The blue eluate was diluted five times and transferred to a smaller column, where sodium and phosphate ions were removed by elution with 0.1 M hydrochloric acid. The blue compound was subsequently eluted with 2 M hydrochloric acid. The solid compound was precipitated with ethanol and ether. Yield: 0.327 g (5.2 %). Anal. $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(H_2O)_2]Cl_4 \cdot 7\ H_2O$: Cr, Cl. $(\varepsilon, \lambda)_{max}$: (270, 532), (112, 394.5). $(\varepsilon, \lambda)_{min}$: (59.4, 442), (45.3, 350). The corresponding dihydroxo complex was obtained by dissolving the compound in an ice-cold solution of ammonia and precipitation with sodium perchlorate at pH = 9.7. The blue-violet compound was washed with a solution of sodium perchlorate (1 M) and with ethanol (96 %). Anal. $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(OH)_2](ClO_4)_2 \cdot 2\ H_2O$: Cr, C, N, H, Cl. $(\varepsilon, \lambda)_{max}$: (242, 559), (182, 378). $(\varepsilon, \lambda)_{min}$: (46.9, 452.5), (122, 352).

4. Di-μ-hydroxo-bis[{bis(2-pyridylmethyl)amine}squaratochromium(III)]ennеahydrate, $[(C_4O_4)(C_{12}H_{13}N_3)Cr(OH)_2Cr(C_{12}H_{13}N_3)(C_4O_4)] \cdot 9\ H_2O$. $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(H_2O)_2]Cl_4 \cdot 7\ H_2O$ (prep. 3) (0.20 g, 0.24 mmol) and squaric acid (0.070 g, 0.61 mmol) were dissolved in water (5 ml). The pH of the solution was adjusted to 3.5 with aqueous sodium hydroxide (2 M). A blue precipitate immediately appeared. The mixture was placed at 55°. The next day large red crystals had separated, and the blue solid had disappeared. The insoluble crystals were washed with water. Yield: 0.030 g (16 %). Anal. $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)_2] \cdot 9\ H_2O$: Cr, C, N, H. It was, however, not possible to locate more than 8 mol of water in the X-ray structure analyses (see below).

5. *fac*-Trichloro{bis(2-pyridylmethyl)amine}chromium(III) monohydrate, *fac*-$[Cr(C_{12}H_{13}N_3)Cl_3] \cdot H_2O$. Red $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)]Br_2 \cdot 2\ H_2O$ (prep. 1) (0.200 g, 0.24 mmol) was suspended in conc. hydrochloric acid (1–2 ml), and the mixture was left in a stoppered flask in the dark for three days. By then green crystals had separated. They were filtered off and washed with hydro-

chloric acid (4 M), water and ethanol (99 %). Yield: 0.115 g (64 %). Anal. $[Cr(C_{12}H_{13}N_3)Cl_3] \cdot H_2O$: C, N, H, Cl. The water content was confirmed by thermogravimetry.

An identical compound was prepared from $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(SO_4)]Cl_2$[7] by the same procedure. The identity of the two sample was established by means of X-ray powder diffraction.

6. *mer*-Trichloro{bis(2-pyridylmethyl)amine}chromium(III) monohydrate, *mer*-$[Cr(C_{12}H_{13}N_3)Cl_3] \cdot H_2O$. Orange-coloured $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)(H_2O)]Cl_2 \cdot 4\ H_2O$ (prep. 2) (0.100 g, 0.124 mmol) was treated with hydrochloric acid as described above. Yield of greenish crystals: 0.070 g (75 %). Anal. $[Cr(C_{12}H_{13}N_3)Cl_3] \cdot H_2O$: C, N, H, Cl. The water content was confirmed by thermogravimetry.

An identical compound was prepared from $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)_2] \cdot 9\ H_2O$ (prep. 4) by the same procedure. The identity of the two samples was established by means of X-ray powder diffraction.

The dihydroxo complex (prep. 3) did not react with conc. hydrochloric acid to give a trichloro complex unless the reaction mixture was heated. In that case, the resulting compound was the *mer*-trichlorotriamine complex, but the reaction could have taken place with change of the amine configuration.

X-ray crystallography. Structure determination. The crystals of di-μ-hydroxo-bis[{bis(2-pyridylmethyl)amine}squaratochromium(III) enneahydrate (prep. 4) form dark-red needles with *a* as the needle axis. The data collection was carried out on an Enraf–Nonius CAD4 diffractometer using graphite monochromated Mo*K*α radiation. Correction for absorption was not applied. Table 1 lists the crystal data and other information relevant to data collection and structure refinement.

The Patterson function gave the position of the chromium atoms, and DIRDIF[10] revealed the hydroxo group, the coordinated oxygen atom from the squarate ion and the atoms in the tridentate ligand apart from the hydrogen atoms. The rest of the atoms in the complex were located by Fourier methods, except for some of the hydrogen atoms for which the positions were calculated. The water molecules were found to be disordered. Only the positions of the oxygen atoms could be located, and only eight oxygen atoms per complex instead of nine as found by elemental analysis as mentioned above. Refinement was carried out anisotropically for all non-hydrogen atoms in the complex. The oxygen atoms from the water molecules were refined isotropically. The X-Ray System[11] was used in the calculations. Coordinates are given in Table 2. A list of thermal parameters and population parameters, and of observed and calculated structure factors can be obtained from the authors on request.

The neutral di-μ-hydroxo complex is centrosymmetric, and the tridentate ligand has the *meridional* configuration and is shown in Figs. 2a and b. The O1 in the squarate ligand is *trans* to one hydroxo group in the double bridge. The complex has an internal hydrogen bond of length 2.63 (3) Å between O2 in the squarate ligand and O0 in the bridging system. The oxygen atom bound to C4 in the squarate ligand was found to be disordered, and two positions, called O4 and O41, were refined both with population factors of 0.5. The distances of these from the plane formed by the four carbon atoms in the squarate ion are both 0.3 Å. The other three oxygens are displaced by 0.1 Å from this plane.

Table 1. Crystal data for $[((C_4O_4)(C_{12}H_{13}N_3)Cr(OH))_2] \cdot 8\ H_2O$.

Space group	Monoclinic $P2_1/n$ (No. 14)
a/Å	10.528(1)
b/Å	19.166(1)
c/Å	14.800(1)
β/°	104.81(1)
V/Å^3	1983
Z	2
μ(Mo*K*α)/cm^{-1}	5.81
Crystal size/mm	0.40×0.18×0.15
Total no. meas. refl. in calc.	3232
sin θ/λ range	0.04–0.58
No. indep. obs. refl.	2801
LT[$F^2 < \sigma^2(F^2)$]	330
No. of parameters	261
R	0.048
R_w	0.072
$w^{-1} = \sigma^2(F) + 0.0117\|F\| + 0.0004\ F^2$	

The oxygen atom O3 opposite to the coordinated atom O1 in the squarate ligand forms a hydrogen bond of length 2.865(5) Å to a neighbouring complex molecule. In this way a puckered net is formed around a plane perpendicular to the glide direction (Fig. 3). The pyridine rings are perpendicualr to this net and parallel to the two-fold axis.

The water molecules are, as mentioned above, partly disordered and placed in the channels formed between the net planes. Only one of these, O1w, can be refined with a population factor of one. It has a contact distance of 3.165 (6) Å to O1 in the complex. The rest are smeared out in groups having oxygen–oxygen distances ranging from 2.2 to 2.8 Å. Distances from these oxygen atoms to O1w are in the range 2.6 to 3.3 Å. The population factors are 0.5 for O2w–O5w and 0.25 for the rest of the water–oxygen atoms. Selected distances and angles are given in Table 3.

Results and discussion

Synthetic and stereochemical aspects. It was demonstrated earlier[7] that chromium(II) sulfate pentahydrate reacts smoothly with bispicam in water to give the dinuclear sulfato-bridged ion $[bispicamCr(OH)_2(SO_4)Crbispicam]^{2+}$ and we now find that chromium(II) squarate dihydrate reacts similarly but gives at least two dinuclear compounds both of which contain one mol of squarate ion per mol. We suggest that one of these compounds has a structure in which two adjacent squarate oxygen atoms are involved in metal bridging, and that the amine ligands surround the

Table 2. Fractional coordinates for $[Cr_2(C_{12}H_{13}N_3)_2(OH)_2(C_4O_4)_2] \cdot 8\ H_2O$.

Atom	x	y	z
Cr	0.92401(5)	0.04851(4)	0.56242(3)
O0	1.0235(2)	−0.0750(2)	0.05535(2)
O1	0.8760(2)	0.0102(2)	0.6775(2)
N0	0.8312(3)	0.1853(2)	0.5576(2)
N11	0.7377(3)	0.0093(2)	0.4838(2)
N12	0.0738(3)	0.1359(2)	0.6433(2)
C21	0.6878(4)	−0.0846(3)	0.4661(2)
C31	0.5633(4)	−0.1026(3)	0.4100(3)
C41	0.4882(4)	−0.0211(4)	0.3692(3)
C51	0.5370(4)	0.0753(4)	0.3886(3)
C61	0.6618(3)	0.0891(3)	0.4472(2)
C71	0.7209(4)	0.1924(3)	0.4724(3)
C22	0.1829(4)	0.1015(3)	0.7037(2)
C32	0.2802(4)	0.1674(4)	0.7521(3)
C42	0.2626(5)	0.2696(4)	0.7372(3)
C52	0.1498(5)	0.3054(3)	0.6794(3)
C62	0.0554(4)	0.2370(3)	0.6324(2)
C72	0.9281(4)	0.2696(3)	0.5661(2)
C1	0.8531(3)	−0.0774(2)	0.7070(2)
C2	0.8702(3)	−0.1820(2)	0.6834(2)
C3	0.8111(3)	−0.2165(3)	0.7585(2)
C4	0.7960(4)	−0.1085(3)	0.7830(2)
O2	0.9159(3)	−0.2265(2)	0.6231(2)
O3	0.7847(3)	−0.2990(2)	0.7874(2)
O4	0.7740(7)	−0.0639(4)	0.8531(4)
O41	0.7284(7)	−0.0682(4)	0.8315(4)
O1 W	0.4720(6)	0.3503(4)	0.3161(4)
O2 W	0.1576(8)	0.4192(7)	0.4331(6)
O3 W	0.0808(9)	0.5081(8)	0.5558(6)
O4 W	0.1479(12)	−0.0237(10)	0.8820(9)
O5 W	0.0734(7)	0.4348(5)	0.3811(5)
O6 W	0.3814(20)	0.3262(15)	0.5041(13)
O7 W	0.4780(16)	0.3584(12)	0.5324(10)
O8 W	0.1762(26)	0.0287(21)	0.9289(20)
O9 W	0.4037(28)	0.3936(24)	0.5564(18)
H N0	0.7960	0.1899	0.6145
H O0	0.0031	0.1242	0.4316
H21	0.7277	0.1394	0.4869
H31	0.5436	−0.1660	0.4080
H41	0.4173	−0.0295	0.3298
H51	0.5127	0.1276	0.3689
H171	0.6621	0.2419	0.4920
H271	0.7571	0.2167	0.4210
H22	0.1956	0.0370	0.6940
H32	0.3321	0.1271	0.7795
H42	0.3340	0.3186	0.7668
H52	0.1258	0.3685	0.6537
H172	0.9455	0.2845	0.4991
H272	0.8938	0.3266	0.5903

chromium atoms in facial positions (Fig. 4a). This assumed structural analogy to the sulfato-bridged compound receives support from a similarity of the absorption spectra, and also from the identity of the reaction products formed with conc. hydrochloric acid. Thus, both compounds react to give the same trichlorotriaminechromium(III) complex, viz. the *facial* form, if the reaction proceeds with retention of the amine configuration (Scheme 1).

When chromium(II) sulfate pentahydrate reacts with bis-

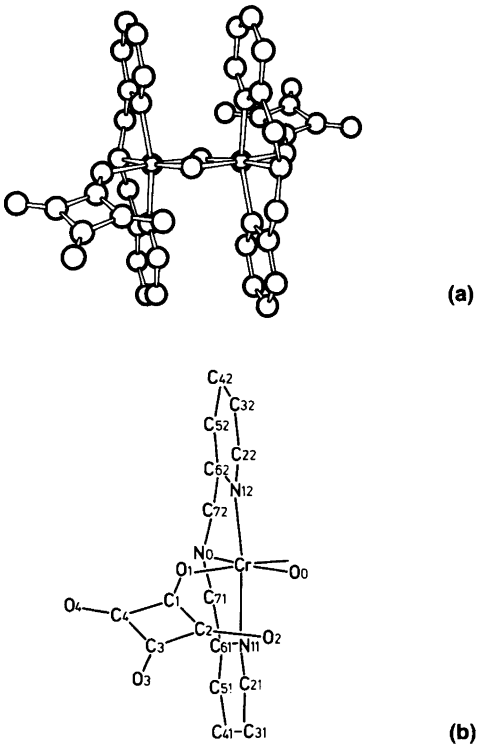

Fig. 2. (a) Drawing and (b) numbering scheme of $[(C_4O_4)(\text{bispicam})Cr(OH)]_2 \cdot 8\ H_2O$. Atom are drawn as 50 % probability ellipsoids.

picam in the presence of barium ions, a dimeric compound with terminal hydroxy groups is formed (see Experimental, prep. 3). The acid form of this compound reacts with sodium sulfate to give the sulfato-bridged dinuclear compound described above.[7] Unexpectedly, the same complex reacts with squaric acid under the same conditions to give an uncharged, dinuclear complex containing two squarate ions as terminal, monodentate ligands and with the amines in *meridional* positions, as confirmed by the X-ray structure determination (Fig. 4c). The product of the reaction of this complex with conc. hydrochloric acid is the *meridional* form of trichlorotriaminechromium(III) if the reaction proceeds with retention of the amine configuration (Scheme 1).

For the product (see Experimental, prep. 2) we suggest a *meridional* configuration of the amine on the basis of the reaction of the compound with conc. hydrochloric acid. This leads to the *meridional* form of trichlorotriaminechromium(III). The squarate ion may occupy a terminal position as a monodentate ligand to one of the chromium atoms (Fig. 4b) or it may function as a bidentate ligand, bridging chromium atoms in different dinuclear units. Both interpretations may result in chain or net-like structures, similar to what is found in the structure described below, since a terminal squarate ion is probably involved in strong hydrogen bonding to ligands on chromium atoms in other molecules (Scheme 1).

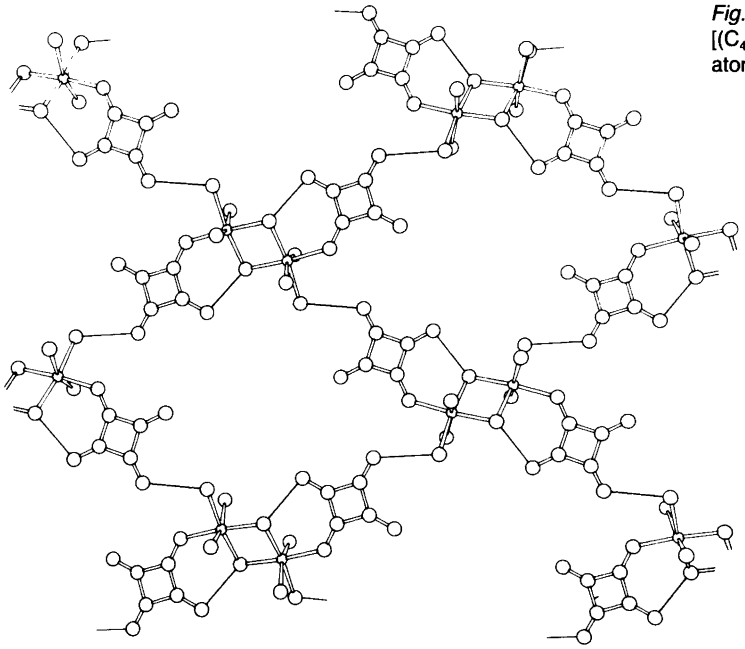

Fig. 3. Simplified drawing showing the hydrogen bonds in $[(C_4O_4)(bispicam)Cr(OH)]_2 \cdot 8\ H_2O$. All carbon and hydrogen atoms in bispicam are omitted.

Table 3. Summary of structural data, selected bond lengths (Å) and angles (°).

$Cr-O_0$	1.957–1.963(2)	O_0-Cr-O_0'	79.2(1)
$Cr-O_1$	1.962(2)	$N_{11}-Cr-N_{12}$	159.2(1)
$Cr-N_0$	2.042(3)	$Cr-O_0-Cr'$	100.8(1)
$Cr-N_{11}$	2.074(3)	$Cr-O_1-C_1$	129.9(2)
$Cr-N_{12}$	2.068(3)		
Pyridine			
C–N	1.341–1.348(4)	C–C–C	118.6–120.3(4)
C–C	1.359–1.394(7)	C–N–C	118.5–119.0(3)
N_0-C_7	1.482–1.491(5)	N–C–C	121.2–122.6(3)
C_6-C_7	1.491–1.503(5)		
Squarate			
C–C	1.442–1.486(5)	C–C–C	88.9–91.2(3)
C–O	1.225–1.278(8)		

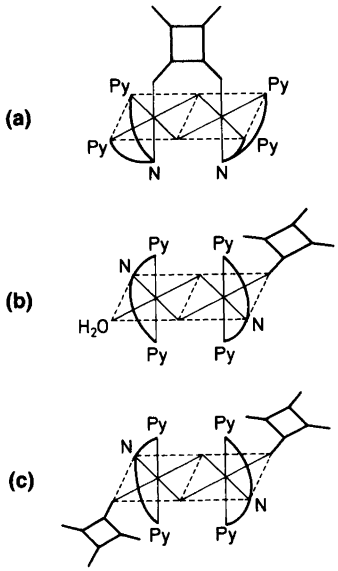

Fig. 4. (a) $[(bispicam)Cr(OH)_2(C_4O_4)Cr(bispicam)]^{2+}$. (b) $[(H_2O)(bispicam)Cr(OH)_2Cr(bispicam)(C_2O_4)]^{2+}$. (c) $[(C_4O_4)(bispicam)Cr(OH)]_2$.

$$Cr(II)SO_4 + bispicam + OH^- + Ba^{2+} \longrightarrow [(OH)bispicamCr(OH)_2Crbispicam(OH)]^{2+} \xrightarrow{+H^+} [(H_2O)bispicamCr(OH)]_2^{4+}$$

$$Cr(II)SO_4 + bispicam + OH^- \longrightarrow [bispicamCr(OH)_2(SO_4)Crbispicam]^{2+}$$

$$Cr(II)C_4O_4 + bispicam + OH^- \longrightarrow [bispicamCr(OH)_2(C_4O_4)Crbispicam]^{2+} \xrightarrow{+HCl} fac\text{-}[CrbispicamCl_3]$$

$$Cr(II)C_4O_4 + bispicam + OH^- \longrightarrow [(H_2O)bispicamCr(OH)_2Crbispicam(C_4O_4)]^{2+} \xrightarrow{+HCl} mer\text{-}[CrbispicamCl_3]$$

$$[(H_2O)bispicamCr(OH)]_2^{4+} + H_2C_4O_4 \longrightarrow [(C_4O_4)bispicamCr(OH)_2Crbispicam(C_4O_4)]$$

Scheme 1.

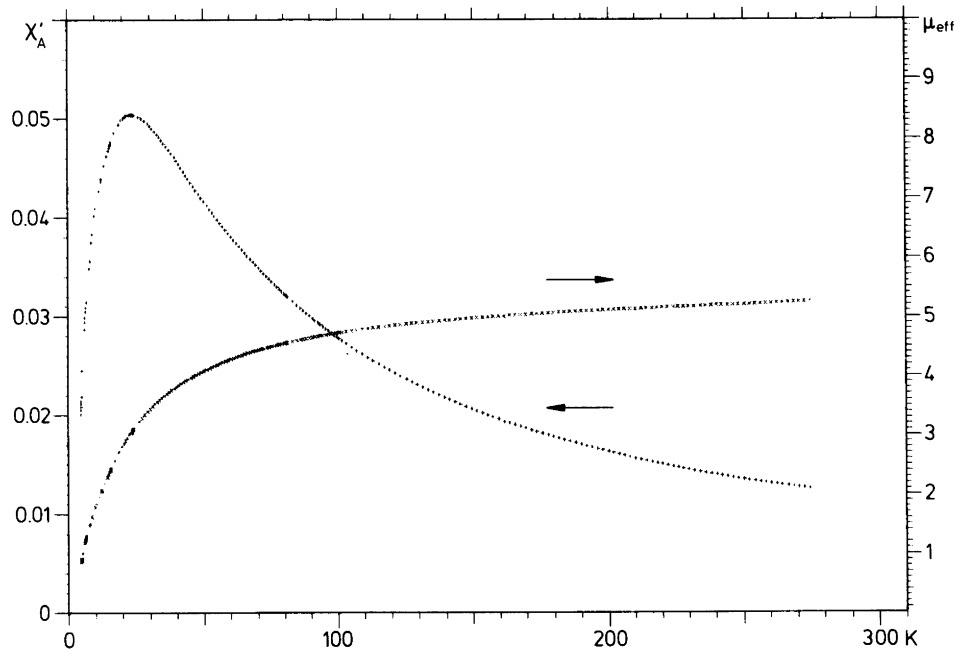

Fig. 5. Magnetic susceptibility (left-hand scale, in cgs units) and effective magnetic moment (right-hand scale, in Bohr magnetons) of $[(C_4O_4)(bispicam)Cr(OH)]_2 \cdot 8\ H_2O$.

Magnetic properties. The magnetic susceptibility and the effective moment of the title compound are shown in Fig. 5, covering the range 4–275 K. These measurements were interpreted in terms of antiferromagnetic two-center interactions according to the Hamiltonian

$$H = J\hat{S}_1 \cdot \hat{S}_2 + \beta g \mathbf{H} \hat{S}.$$

Data fitting was performed according to a least-squares method as previously described.[8] The resultant parameter values were $J = 10.53(5)$ cm^{-1} and $g = 1.986(3)$. The value of J equals the triplet energy relative to the singlet ground state. The data fitting showed no indication of any significant interdimer interaction via the squarate ligands and hydrogen bonds throughout the sheet illustrated in Fig. 4.

The value of J can be correlated with the structural information via the GHP model[12] for magnetic exchange between d^3 centres bridged by OH groups. We used the average value of the Cr–O distances, $r = 1.960(3)$ Å, and the angle Cr–O–Cr = $\Phi = 100.7(2)°$, and, finally, a value of $\Theta = 43°$ was calculated as the angle between the OH vector and the plane through Cr–O–Cr–O. With these input parameters the calculated value of J was $J_{calc} = J_a - J_f = 16.3 - 5.2 = 11.1$ cm^{-1}. Here, J_a and J_f are antiferromagnetic and ferromagnetic contributions, respectively. An estimated standard deviation for J_{calc} cannot be given since the positions of the hydrogen atoms were not refined. The contribution from r and Φ is ± 0.7 cm^{-1}.

On this background the structural and magnetic properties are in satisfactory agreement according to the GHP model.

The compounds described in prep. 1 and 2 in the Experimental exhibit antiferromagnetic exchange interactions as expected for dinuclear chromium(III) complexes with coupling constants of $J = 15.45(6)$ cm^{-1} and 19.54(5) cm^{-1}, respectively. These results will not be discussed further since structural information is not yet available.

References

1. Habenschuss, M. and Gerstein, B. S. *J. Chem. Phys. 61* (1974) 854.
2. Weiss, A., Riegler, E., Alt, J., Böhme, H. and Roll, C. *Z. Naturforsch. 41 B* (1986) 18.
3. Van Ooijen, J. A. C., Reedikj, J. and Spek, A. L. *Inorg. Chem. 18* (1979) 1184.
4. Soules, R., Dahan, F., Laurent, J. P. and Castan, P. *J. Chem. Soc., Dalton Trans.* (1988) 587.
5. Chesick, J. P. and Doany, F. *Acta Crystallogr., Sect. B 37* (1981) 1076.
6. Michelsen, K., Nielsen, K. M. and Pedersen, E. *Acta Chem. Scand., Ser. A 42* (1988) 724.
7. Larsen, S., Michelsen, K. and Pedersen, E. *Acta Chem. Scand., Ser. A 40* (1986) 63.
8. Andersen, P., Damhus, T., Pedersen, E. and Petersen, A. *Acta Chem. Scand., Ser. A 38* (1984) 359.
9. Josephsen, J. and Pedersen, E. *Inorg. Chem. 16* (1977) 2534.
10. Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, T. E. M., Prick, P. A., Noordik, J. H., Beurskens, G. and Patharsarthi, W. *DIRDIF: Direct Methods for Difference Structures,* Technical Report 1981/2, Crystallography Laboratory, Toernooiveld, Nijmegen, The Netherlands 1981.
11. Stewart, J. M., Machin, P. H., Dickinson, C., Ammon, H. L. and Flack, H. L. *The X-Ray System. Version 1976,* Technical Report TR 446, Computer Science Center, University of Maryland, College Park, MD 1976.
12. Glerup, J., Hodgson, D. J. and Pedersen, E. *Acta Chem. Scand., Ser. A 37* (1983) 161.

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