

# Synthesis and Magnetic Characterization of Salts of the Dimeric Chromium(III) Cation $\mu$ -sulfato-di- $\mu$ -hydroxo-bis[ $\{N,N'$ -bis(2-pyridylmethyl)-amine $\}$ chromium(III)]. Crystal Structure of the Dithionate Salt, $[(\text{bispicam})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{bispicam})](\text{S}_2\text{O}_6) \cdot 3 \text{H}_2\text{O}$

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A new dimeric Cr(III) complex with one bidentate sulfate and two hydroxide ions as bridging ligands was synthesized. The tridentate ligand  $N,N'$ -bis(2-pyridylmethyl)-amine occupies the remaining coordination sites. A new trimeric complex is obtained as a by-product. The crystal structure of the dithionate salt,  $[(\text{bispicam})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{bispicam})]\text{S}_2\text{O}_6 \cdot 2.8 \text{H}_2\text{O}$  was determined from low-temperature X-ray diffraction data. The complex crystallizes in the monoclinic space group  $P2_1/c$  with 4 dinuclear formula units in a cell of dimensions  $a = 13.191(2)$ ,  $b = 22.119(3)$ ,  $c = 11.479(6)$  Å, and  $\beta = 92.58(3)^\circ$  at 105 K. The structure was refined by full-matrix least-squares methods to  $R_w = 0.047$  based on 7965 independent reflections. The fragment consisting of the two Cr atoms and the bridging hydroxo groups deviates from planarity, which leads to a Cr1-Cr2 separation of 2.9157(6) Å. Around each chromium the pyridine parts of the amine ligand are *cis* to each other and *trans* to the bridging hydroxo ligands. The over-all symmetry of the cation could ideally have been  $C_{2v}$  (meso), but is only close to  $C_s$  (meso). The magnetic susceptibility in the temperature range 4–300 K indicates intramolecular antiferromagnetic exchange. The susceptibility data were fitted to a model assuming independent triplet, quintet and septet energies. The results were 14.4(1), 27.0(1) and 46.5(2)  $\text{cm}^{-1}$ , respectively. A statistical  $V^2$  test showed that the data are inconsistent with the Landé rule as expressed by the Heisenberg Hamiltonian according to which the energy ratios are 1:3:6. Our results are close to 1:2:3. The structural parameters were used to calculate the triplet energy on the basis of the semiempirical Glerup-Hodgson-Pedersen (GHP) model for hydroxo and oxo bridged dimers and lead to a calculated value of 15(3)  $\text{cm}^{-1}$ , in agreement with the data fitting. This result is based on the assumption that the bridging sulfate ion gives a negligible contribution to the metal-to-metal orbital overlaps. The serious deviation from the Landé rule may indicate that a simplifying assumption regarding interelectronic repulsion in the GHP model does not hold in this particular Cr(III) dimer and in few other cases with short metal-metal distances.

Dinuclear chromium(III) complexes with hydroxo groups as bridging ligands have been studied extensively due to their spectroscopic, mag-

netic and structural properties.<sup>1–45,53</sup> Particular emphasis has been placed on attempts to correlate the spectral and magnetic properties of these complexes with specific structural features. Compounds of this type and containing pyridyl sub-

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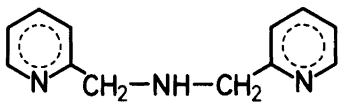


Fig. 1.  $N,N'$ -bis(2-pyridylmethyl)amine,  $C_{12}H_{13}N_3$ , bispicam.

stituted bidentate<sup>16,23,32,36</sup> and tetradentate<sup>19,28,41,44</sup> ligands have been included in our previous investigations. As an extension of this work chromium(III) complexes with the tridentate ligand  $N,N'$ -bis(2-pyridylmethyl)-amine (bispicam), Fig. 1, are being investigated.

This paper reports the synthesis and the characterizations by magnetic, spectroscopic and X-ray diffraction methods of such a dimeric complex with two bridging hydroxo groups and one bridging sulfato group. Cases of anions acting as bidentate bridging ligands have been observed previously. Thus the  $\mu$ -sulfato group first appeared in  $\Delta, \Lambda$ - $\mu$ -hydroxo- $\mu$ -sulfato-bis[bis(ethylenediamine)chromium(III)] ion investigated by Springborg<sup>24</sup> and Kaas.<sup>25</sup> The  $\mu$ -carbonato group recently appeared in  $\mu$ -carbonato-di- $\mu$ -hydroxo-bis[(1,4,7-triazacyclononane)-chromium(III)] iodide as described by Wieghardt and coworkers.<sup>31</sup>

Another oligomeric complex containing the bispicam ligand was obtained in the synthetic procedure. The structure of the compound is unknown. The analytical, spectroscopic and magnetic properties, however, indicate that the compound is trimeric and contains four bridging hydroxo groups and a terminal sulfato group.

## Experimental

**Reagents.** Pyridine-2-carboxaldehyde and 2-pyridylmethylamine were purchased from Fluka AG. SP-Sephadex C-25 was purchased from Pharmacia, Uppsala, Sweden. All other compounds were of reagent grade and were used without further purifications.

**Analyses.** 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, sulphur and halogen analyses by standard methods.

**Physical Measurements.** Absorption spectra were recorded on a Cary Model 14 spectrophotometer. The spectra are characterized by their maxima and minima ( $\epsilon, \lambda$ ) where the molar extinction coefficient  $\epsilon$  is in units of  $l \text{ mol}^{-1} \text{ cm}^{-1}$  and  $\lambda$  is in nm. The compounds were dissolved in 0.1 M hydrochloric acid. 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 12000  $\text{\AA}$ .  $\text{Hg}[\text{Co}(\text{NCS})_4]$  was used as a calibrant<sup>46</sup> for susceptibility at room temperature. The temperature scale below 77 K was calibrated using a solid solution of 1 mol % hexamminchromium(III) ions in hexammincobalt(III) iodide.<sup>40</sup> Diamagnetic corrections were made using Pascal constants. Preliminary descriptions of the apparatus are found elsewhere.<sup>22</sup>

## Preparations

1.  $N,N'$ -bis(2-pyridylmethyl)-amine, trihydrochloride, monohydrate,  $C_{12}H_{13}N_3 \cdot 3\text{HCl} \cdot \text{H}_2\text{O}$  (abbrev. for the amine, bispicam).

Pyridine-2-carboxaldehyde (21.4 g, 0.2 mol) was dissolved in ethanol (100 ml, 99%). 2-pyridylmethylamine (21.6 g, 0.2 mol) was added dropwise while stirring followed by sodium tetrahydridoborate (15 g, 0.4 mol) in small portions. The stirring was continued for 2½ h at room temperature. Then the filtered, ice-cooled solution was acidified (pH = 4) with hydrochloric acid (12 M). Filtering. To the ice-cooled filtrate was added hydrochloric acid (12 M) to strong acid reaction, ethanol (600 ml, 99%) and ether (200 ml). The solid was filtered and washed with ethanol (99%, 0°). Yield: 40 g (61%). The crude product was dissolved in hydrochloric acid (20 ml, 4 M) and reprecipitated with ethanol (40–50 ml, 99%). Yield: 33 g. Anal.  $C_{12}H_{13}N_3 \cdot 3 \text{HCl} \cdot \text{H}_2\text{O}$ : C, N, H, Cl.

2.  $\mu$ -Sulfato-di- $\mu$ -hydroxo-bis[ $\{N,N'$ -bis(2-pyridylmethyl)-amine}chromium(III)] chloride,  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2(\text{OH})_2(\text{SO}_4)]\text{Cl}_2 \cdot 5-6 \text{H}_2\text{O}$ .

Bispicam. 3 HCl · H<sub>2</sub>O (3.40 g, 10.4 mmol) was dissolved in a solution of sodium hydroxide in water (2 M, 14.8 ml). Crushed chromium(II) sulfate, pentahydrate (2.4 g, 10 mmol) was added while stirring. The colour of the solution changed rapidly from blue to red. After 3–4 h sodium perchlorate (~3 g) was added to precipitate a crude product consisting mainly of a dimeric and a tri-

meric compound. The solid was washed with ethanol and dissolved in water. The solution was transferred to two (capacity problems) Sephadex columns ( $l = 16$  cm,  $d = 4$  cm) and eluted with a phosphate solution (0.05 M  $\text{Na}_2\text{HPO}_4 - 0.05$  M  $\text{NaH}_2\text{PO}_4$ ). Two relatively fast moving bands appeared on each column, a red with a bluish tint and a red-brown. The coloured eluates were diluted 10 times and transferred to shorter columns where sodium and phosphate ions were eluted with 0.1 M hydrochloric acid and the compounds afterwards with 2 M hydrochloric acid. Eluates of the same kind were combined, and the compounds were precipitated with ethanol and ether. The red compound isolated from bd. 1 consisted of a dimeric compound, the red-brown of a trimeric (see below, prep. 6) Bd. 1. Red compound. Yield: 10 g (~25 % based on chromium(II)). The compound is not completely homogeneous. (Found: Cr 12.82; C 35.38; N 10.54; H 4.44; S 4.04; Cl 9.06. Calc. for  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2(\text{OH})_2(\text{SO}_4)]\text{Cl}_2 \cdot 5.5 \text{H}_2\text{O}$ : Cr 12.96; C 35.92; N 10.47; H 4.90; S 4.00; Cl 8.84).

3.  $\mu$ -Sulfato-di- $\mu$ -hydroxo-bis[ $\{\text{N},\text{N}'\text{-bis}(2\text{-pyridylmethyl})\text{-amine}\}$ chromium(III)] perchlorate,  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2(\text{OH})_2(\text{SO}_4)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ .

A pure perchlorate was obtained when a conc. solution (2 g in 1 ml) of sodium perchlorate was added to a solution of the red chloride (0.25 g, 0.31 mmol) in water (12 ml). After cooling on ice the red precipitate was filtered and washed with ethanol (96 %). Yield: 0.24 g (91 %). Recrystallization from boiling water was accompanied by a loss of 25 %. Anal.  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2(\text{OH})_2(\text{SO}_4)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ : Cr, C, N, H, S, Cl. In other cases the compound crystallized with 1.5 or 2 moles of crystal water.  $(\epsilon, \lambda)_{\text{max}}$ : (86.7, 535.5), (89.8, 392).  $(\epsilon, \lambda)_{\text{min}}$ : (24.3, 448), (35.4, 353).

4.  $\mu$ -Sulfato-di- $\mu$ -hydroxo-bis[ $\{\text{N},\text{N}'\text{-bis}(2\text{-pyridylmethyl})\text{-amine}\}$ chromium(III)] iodide,  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2(\text{OH})_2(\text{SO}_4)]\text{I}_2 \cdot 6 \text{H}_2\text{O}$ .

An iodide was obtained when a conc. solution (0.5 g in 1 ml) of sodium iodide was added to a solution of the red chloride (0.30 g, 0.37 mmol) in water (4 ml). After cooling on ice the precipitate was filtered and washed with a solution of sodium iodide (2 M) and with ethanol (99 %, 0°). Yield: 0.33 g (90 %). Recrystallization from a small amount of boiling water was accompanied by a loss of 33 %. Anal.  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2$

$(\text{OH})_2(\text{SO}_4)]\text{I}_2 \cdot 6 \text{H}_2\text{O}$ : Cr, C, N, H, I.  $(\epsilon, \lambda)_{\text{max}}$ : (86.6, 535.5), (91.5, 392).  $(\epsilon, \lambda)_{\text{min}}$ : (24.9, 448), (38.7, 353.5).

5.  $\mu$ -Sulfato-di- $\mu$ -hydroxo-bis[ $\{\text{N},\text{N}'\text{-bis}(2\text{-pyridylmethyl})\text{-amine}\}$ chromium(III)] dithionate,  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2(\text{OH})_2(\text{SO}_4)]\text{S}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$  (2.8  $\text{H}_2\text{O}$ ).

A dithionate was obtained when the red chloride (0.40 g, 0.50 mmol) was added to a saturated water solution (3 ml) of lithium dithionate. The precipitate that formed immediately was filtered and washed with ethanol (96 %). Recrystallization from boiling water (3–4 ml) gave coarse crystals that were washed with ethanol (67 %). Yield: 0.15 g (35 %). Anal.  $[\text{Cr}_2(\text{C}_{12}\text{H}_{13}\text{N}_3)_2(\text{OH})_2(\text{SO}_4)](\text{S}_2\text{O}_6) \cdot 3 \text{H}_2\text{O}$ : Cr, C, N, H, S.  $(\epsilon, \lambda)_{\text{max}}$ : (88.2, 535.5), (91.7, 392.5).  $(\epsilon, \lambda)_{\text{min}}$ : (25.0, 449), (37.0, 354).

6.  $\mu$ -[*cis*-Dihydroxo-sulfato $\{\text{N},\text{N}'\text{-bis}(2\text{-pyridylmethyl})\text{-amine}\}$ chromium(III)] di- $\mu$ -hydroxo-bis[ $\{\text{N},\text{N}'\text{-bis}(2\text{-pyridylmethyl})\text{-amine}\}$ chromium(III)] perchlorate,  $[\text{Cr}_3(\text{C}_{12}\text{H}_{13}\text{N}_3)_3(\text{OH})_4(\text{SO}_4)](\text{ClO}_4)_3 \cdot 5 \text{H}_2\text{O}$ .

See prep. 2: 2. bd. Yield: 1.2 g of an inhomogeneous red-brown chloride.

A pure perchlorate was obtained when a saturated solution of sodium perchlorate (2 ml) was added to a solution of the red-brown chloride (1.2 g) dissolved in water (7 ml). After cooling on ice and filtering the precipitate was washed with ethanol (96 %). Yield: 1.18 g (18 % based on chromium(II)). 50 % was lost by recrystallization from boiling water. Anal.  $[\text{Cr}_3(\text{C}_{12}\text{H}_{13}\text{N}_3)_3(\text{OH})_4(\text{SO}_4)](\text{ClO}_4)_3 \cdot 5\text{H}_2\text{O}$ : Cr, C, N, H, S, Cl.  $(\epsilon, \lambda)_{\text{max}}$ : (210, 528), (277, 404).  $(\epsilon, \lambda)_{\text{min}}$ : (91.3, 461.5), (85.9, 348).

*Crystallographic Examination.* The compound crystallizes as red irregular shaped crystals which were assigned to the monoclinic system on the basis of precession and Weissenberg photographs. The systematically absent reflections  $h0l$  for  $l = 2n + 1$  and  $0k0$  for  $k = 2n + 1$  uniquely determine the space group to be  $P2_1/c$ .

Diffraction data were obtained from a single crystal with the dimensions  $0.20 \times 0.25 \times 0.50$  mm. The data were collected with an Enraf-Nonius CAD-4-diffractometer using  $\text{MoK}\alpha$  radiation monochromatized from a highly mosaic graphite crystal. The crystal was cooled to ca. 105 K dur-

Table 1.

Space group	$P2_1/c$ , monoclinic
Temperature	105 K
Cell constants at 105 K	$a = 13.191(2) \text{ \AA}$ $b = 22.119(3) \text{ \AA}$ $c = 11.479(6) \text{ \AA}$ $\beta = 92.58^\circ(3)$ $v = 3346(3) \text{ \AA}^3$
Molecular formula	$\text{Cr}_2\text{C}_{24}\text{H}_{33.6}\text{N}_6\text{O}_{14.8}\text{S}_3$
Molecular weight	843.15 $\text{g mol}^{-1}$
Molecules/cell	$Z = 4$
Calculated density (105 K)	1.674 $\text{g cm}^{-3}$
Radiation	$\text{MoK}\alpha$ , $\lambda = 0.71073 \text{ \AA}$
Linear absorption coefficient	8.89 $\text{cm}^{-1}$
Data collection range	$\pm hkl$ ( $1^\circ \leq \theta \leq 30^\circ$ ) $\pm hk-l$ ( $1^\circ \leq \theta \leq 16^\circ$ )
Scan width	$\Delta\theta = 1.00 + 0.35 \tan\theta$
Maximum scan time	120 s.
Scan speed range in $\theta$	0.91–4.02 $\text{deg min}^{-1}$
Residuals from averaging of symmetry related reflections	$R = 0.0187$ $R_w = 0.0305$
Number of independent reflections	9726
Independent reflections with $I/\sigma(I) \geq 2.0$	7965
Number of variables	553
Final residuals	
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.043
$R_w = \{ \sum w( F_o  -  F_c )^2 / \sum w F_o ^2 \}^{1/2}$	0.047

ing the data collection by an Enraf-Nonius low-temperature device. The temperature close to the crystal measured with a thermocouple showed variations within  $\pm 0.5$  K. The cell parameters were determined from a least squares refinement of the setting angles of 16 high angle reflections. The diffractometer was operated in the  $\omega-2\theta$  scan mode. The intensities of two standard reflections were measured after every 10000 s during the data collection and showed no systematic variations. After every 200 reflections the orientation of the crystal was checked.

Data processing included corrections for Lorentz-polarization and background effects, but no correction for absorption. The symmetry related reflections were averaged; standard deviations for the measured intensities were based on counting statistics. The crystal data and other informa-

tion pertinent to data collection and refinement are listed in Table 1.

**Structure Solution and Refinement.** The structure was solved by Patterson and Fourier methods. The positions for the two chromium atoms were deduced from the Patterson function and the remaining non-hydrogen atoms were located after subsequent least squares iterations and difference electron density calculations. Isotropic least squares refinement of these atoms converged at a conventional  $R$ -value of 0.069; when anisotropic thermal parameters were introduced for the chromium and sulfur atoms this value was reduced to 0.067. After anisotropic thermal parameters were introduced for the other non-hydrogen atoms in the structure the conventional  $R$ -value dropped to 0.057. A difference density calculated after this refinement showed that the position for one of the water molecules (O5) is partly populated and it was impossible to localize the hydrogen atoms bonded to this oxygen atom. The positions for the other hydrogen atoms in the structure were very clearly indicated in this difference density.

The positions for the hydrogen atoms were included in the refinement but they were given a common isotropic thermal parameter,  $U = 0.04 \text{ \AA}^2$ . The population parameter for O5 was also included in the refinement cycles where the weights were changed from unit weights of the form  $w^{-1} = \sigma^2(F) + 10^{-4}|F|^2$ . This refinement converged with the values for  $R$  and  $R_w$  of 0.045 and 0.048, respectively. A difference density calculated at this stage contained a large peak of  $1.5 \text{ e/\AA}^3$  which was interpreted as another partly populated water position. This water molecule (O6) was included in the refinement with an isotropic temperature factor. Alternating refinements of the population parameters and thermal parameters for O5 and O6 were performed. In the final refinement cycles all the parameters were allowed to vary. The maximum shift was  $0.18\sigma$ . The final difference density was featureless with a maximum peak of  $0.6 \text{ e/\AA}^3$ . The population parameters obtained from the least squared refinement showed that the compound crystallizes with 2.8  $\text{H}_2\text{O}$  per formula unit in reasonable agreement with the chemical analysis which had suggested 3  $\text{H}_2\text{O}$ . The final residuals are  $R = 0.043$  and  $R_w = 0.047$ . An inspection of the data

Table 2. [(bispicam)Cr(OH)<sub>2</sub>(SO<sub>4</sub>)Cr(bispicam)]S<sub>2</sub>O<sub>6</sub> · 2.8 H<sub>2</sub>O. Final fractional coordinates and  $U_{iso}$ \*

ATOM	x	y	z	$U_{iso}$
<b>Cation</b>				
Cr1	0.85803(2)	0.14215(2)	0.20502(3)	0.0089
Cr2	0.63735(2)	0.13899(2)	0.21079(3)	0.0088
O1	0.74551(12)	0.09478(7)	0.13546(14)	0.0115
O2	0.75287(11)	0.16361(7)	0.30949(13)	0.0102
N11	0.96979(14)	0.19185(8)	0.2909(2)	0.0115
C12	1.0136(2)	0.24185(11)	0.2491(2)	0.0166
C13	1.0897(2)	0.27204(12)	0.3121(2)	0.0213
C14	1.1190(2)	0.25064(12)	0.4219(3)	0.0218
C15	1.0751(2)	0.19873(11)	0.4643(2)	0.0170
C16	1.0004(2)	0.16982(10)	0.3957(2)	0.0121
C17	0.9463(2)	0.11301(11)	0.4310(2)	0.0139
N20	0.91646(14)	0.07891(9)	0.3229(2)	0.0117
C27	1.0036(2)	0.04483(11)	0.2770(2)	0.0153
C26	1.0228(2)	0.06105(11)	0.1532(2)	0.0148
C25	1.0983(2)	0.03230(12)	0.0920(2)	0.0204
C24	1.1080(2)	0.04607(12)	-0.0243(3)	0.0236
C23	1.0452(2)	0.08952(12)	-0.0775(2)	0.0219
C22	0.9746(2)	0.11788(11)	-0.0110(2)	0.0177
N21	0.96353(14)	0.10367(9)	0.1020(2)	0.0130
N31	0.53267(14)	0.18077(8)	0.3111(2)	0.0118
C32	0.4764(2)	0.22953(11)	0.2811(2)	0.0162
C33	0.4046(2)	0.25268(11)	0.3531(2)	0.0206
C34	0.3910(2)	0.22447(12)	0.4592(2)	0.0210
C35	0.4482(2)	0.17398(11)	0.4903(2)	0.0164
C36	0.5186(2)	0.15307(10)	0.4138(2)	0.0113
C37	0.5846(2)	0.09840(10)	0.4369(2)	0.0126
N40	0.60423(14)	0.06980(8)	0.3227(2)	0.0109
C47	0.5173(2)	0.03208(11)	0.2779(2)	0.0148
C46 <sup>†</sup>	0.4797(2)	0.05084(10)	0.1581(2)	0.0131
C45	0.4039(2)	0.01825(11)	0.0967(2)	0.0177
C44	0.3732(2)	0.03697(12)	-0.0138(2)	0.0199
C43	0.4155(2)	0.08830(12)	-0.0610(2)	0.0196
C42	0.4899(2)	0.11881(11)	0.0039(2)	0.0161
N41	0.52221(14)	0.10009(9)	0.1112(2)	0.0123
S1	0.73463(4)	0.24148(2)	0.05565(5)	0.0119
O11	0.83046(12)	0.20993(7)	0.09704(14)	0.0144
O12	0.64652(12)	0.21010(7)	0.10754(14)	0.0145
O13	0.72408(13)	0.23448(8)	-0.07124(14)	0.0172
O14	0.73800(13)	0.30401(7)	0.0912(2)	0.0185
<b>Anion</b>				
S2	0.22207(4)	0.07788(2)	-0.34146(5)	0.0116
S3	0.25672(4)	0.04530(2)	-0.51042(5)	0.0126
O21	0.24825(13)	0.02576(8)	-0.26767(14)	0.0186
O22	0.28505(14)	0.13055(8)	-0.3185(2)	0.0209
O23	0.11373(12)	0.09035(8)	-0.3480(2)	0.0185
O31	0.22315(13)	0.09088(8)	-0.5940(2)	0.0193
O32	0.36537(12)	0.03534(8)	-0.5018(2)	0.0179
O33	0.19765(14)	-0.01071(8)	-0.5177(2)	0.0231
<b>Water Molecules</b>				
O3	0.1687(2)	0.90598(10)	0.2965(2)	0.0258
O4	0.2782(2)	0.60835(9)	0.6020(2)	0.0211
O5(0.69(1))	0.2536(4)	0.1557(2)	0.1792(4)	0.0585
O6(0.11(1))	0.4272(14)	0.8669(9)	0.280(2)	0,030(6)

\* $U_{iso}$  is calculated as  $\frac{1}{3} \sum_i \sum_j U_{ij} \bar{a}_i \cdot \bar{a}_j$ ,  $a_i^* a_j^*$  for the atoms refined with anisotropic thermal parameters.

showed that these do not suffer from the effects of secondary extinction.

The SDP-system<sup>47</sup> was used in the initial structure solution. The X-ray<sup>48</sup> system was employed for the final refinements and crystallographic computations and ORTEP II<sup>49</sup> for the illustrations. The atomic scattering factors used in calculations were those tabulated by Cromer and Mann<sup>50</sup> except for hydrogen where the values by Stewart *et al.*<sup>51</sup> were used. The anomalous scattering corrections added to the scattering factors of Cr and S were calculated by Cromer and Liberman.<sup>52</sup>

The positional parameters derived from the final least-squares cycle with their standard deviations are listed in Table 2. The thermal parameters, positional parameters for the hydrogen atoms as well as a list of observed and calculated structure amplitudes may be obtained from one of the authors (S.L.).

## Results and Discussion

### Synthetic Aspects

Chromium(II) sulfate pentahydrate reacts smoothly with bispicam in water to give the previously unknown ion  $[(\text{bispicam})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{bispicam})]^{2+}$  and a trinuclear complex ion as a byproduct. The reaction is easy to attend because it is followed by a colour change from blue to bright red. The same two compounds can be obtained by the reaction of chromium(III) sulfate pentahydrate and the amine in question in the presence of zinc dust or chromium(II) but the yields are lower.

In forthcoming publications the general utility of the former method will be exemplified by several other dimeric complexes containing bispicam and two or three bridging ligands and produced by substitution of other chromium(II) compounds for chromium(II) sulfate.

### Stereochemistry of the Compounds

The binuclear ion  $[(\text{bispicam})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{bispicam})]^{2+}$  with three bridging ligands between the chromium atoms exists, in principle, in several different isomeric forms owing to geometrical and configurational isomerism. Fig. 2a and 2b represent meso-forms of the symmetries  $C_{2v}$  and  $C_s$  in the ideal cases. An isomer with an

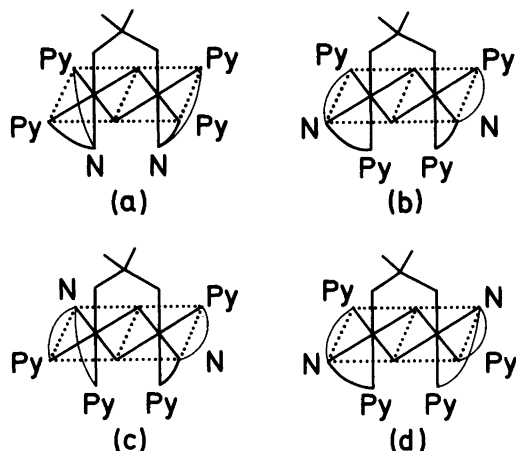


Fig. 2. Geometrical isomers of  $[(\text{bispicam})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{bispicam})]^{2+}$ .

a. Meso- $(C_{2v})$

b. Meso- $(C_s)$

c. and d. The enantiomeric pair,  $\Delta\Delta$  and  $\Lambda\Lambda$ .

amine configuration as shown in Fig. 2b is unlikely to exist because the hydrogen atoms on ligand molecules attached to different metal ions are very close. The racemate consisting of an equimolar mixture of the enantiomers depicted on Fig. 2c and 2d may exist but we have not detected them in this system.

The analytical and magnetic data for the byproduct indicate that this compound is a trinuclear complex. A schematic representation of

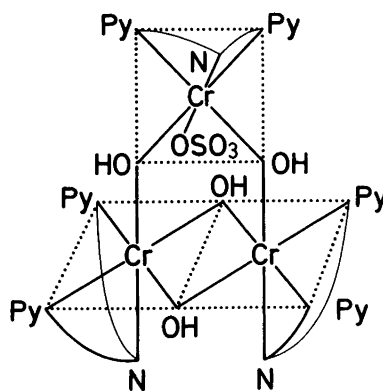


Fig. 3. An example of a trinuclear chromium(III) complex with the formula  $[\text{Cr}_3(\text{bispicam})_3(\text{OH})_3(\text{SO}_4)]^{3+}$ .

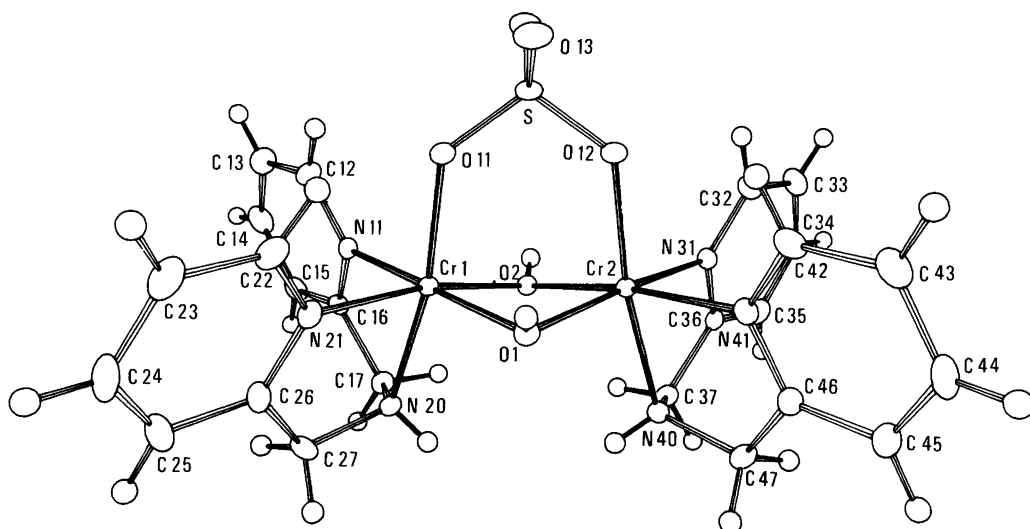


Fig. 4. An ORTEP drawing of the  $[(\text{bispicam})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{bispicam})]^{2+}$  cation showing the atomic labelling. The thermal ellipsoids of the atoms enclose 50 % probability. Hydrogen atoms are drawn as spheres with a radius of 0.1 Å.

such a complex ion containing chromium, bispicam and sulfate in the molar ratios 3:3:1 and with a charge of 3 is shown in Fig. 3. Preliminary results from the magnetic measurements indicate that two of the chromium atoms are equivalent but different from the third. This implies that the sulfate group is bound either to two chromium atoms or to one. The second configuration is most probable because the first would be tantamount to the existence of a terminal hydroxo group on the third chromium atom and this is not likely judging from the spectroscopic results (see below).

#### Description of the Crystal Structure

The structure is formed by binuclear cations, dithionate ions and water molecules that interact by a system of hydrogen bonds.

The binuclear cation as observed in the crystal is shown in Fig. 4. The pyridine parts of the ligands are *trans* to one of the bridging hydroxo groups and *cis* to the other.

The over-all geometry of the cation conforms with the meso form shown in Fig. 2a. An inspection of the bond lengths, bond angles and torsion angles given in Table 3 shows that the over-all symmetry of the cation is close to  $C_2$  with a non-

crystallographic mirror plane through S1, O1 and O2. It is remarkable that the Cr1, O1, O2, Cr2 moiety deviates quite significantly from planarity. Table 4 lists the deviations from the least squares plane calculated for this group of atoms. The interplanar angle between the Cr1, O1, O2 and Cr2, O1, O2 plane is  $23^\circ$ . This reduces the Cr1-Cr2 separation to 2.9157(6) Å. In di- $\mu$ -hydroxo bridged chromium complexes with a planar Cr1, Cr2, O1, O2 group the Cr-Cr distances reported are in the range 2.950–3.059 Å.<sup>20,21,25,26,32,37,53</sup>

The six independent Cr-N distances are of similar magnitude, 2.049 Å to 2.071 Å. These results are consistent with the Cr-N distances found in related complexes.<sup>9,10,12,21,25,32</sup> The four pyridine rings are planar within the experimental accuracy, the interplanar angles between these groups are all very close to  $90^\circ$ . This arrangement with internally perpendicular pyridine groups minimizes the interactions between the groups. The angles between the pyridine groups and the average coordination plane (Cr1, O1, O2, Cr2) are in the range  $67^\circ$ – $70^\circ$ , which illustrated that this part of the ligand is slightly twisted away from the sulfato group. The distances involving the bridging sulfato group are almost identical to those observed in the  $\mu$ -hydroxo- $\mu$ -sulfato-bis(bis(ethyle-

Table 3. Bond lengths (Å), bond angles (deg) and torsion angles (deg).

Cr1 – O1	1.958(2)	Cr2 – O2	1.936(2)
Cr1 – O2	1.933(2)	Cr2 – O1	1.962(2)
Cr1 – O11	1.969(2)	Cr2 – O12	1.976(2)
Cr1 – N11	2.055(2)	Cr2 – N31	2.057(2)
Cr1 – N20	2.071(2)	Cr2 – N40	2.058(2)
Cr1 – N21	2.051(2)	Cr2 – N41	2.049(2)
N11 – C12	1.346(3)	N31 – C32	1.346(3)
C12 – C13	1.382(4)	C32 – C33	1.383(4)
C13 – C14	1.386(4)	C33 – C34	1.387(4)
C14 – C15	1.384(4)	C34 – C35	1.386(4)
C15 – C16	1.389(3)	C35 – C36	1.386(3)
C16 – N11	1.344(3)	C36 – N31	1.348(3)
C16 – C17	1.509(3)	C36 – C37	1.507(3)
C17 – N20	1.489(3)	C37 – N40	1.488(3)
N20 – C27	1.490(3)	N40 – C47	1.491(3)
C27 – C26	1.498(3)	C47 – C46	1.499(3)
C26 – N21	1.343(3)	C46 – N41	1.348(3)
N21 – C22	1.349(3)	N41 – C42	1.350(3)
C22 – C23	1.381(4)	C42 – C43	1.381(3)
C23 – C24	1.392(4)	C43 – C44	1.386(4)
C24 – C25	1.380(4)	C44 – C45	1.378(4)
C25 – C26	1.397(3)	C45 – C46	1.396(3)
S1 – O11	1.502(2)	S1 – O12	1.500(2)
S1 – O13	1.465(2)	S1 – O14	1.442(2)
S2 – O21	1.463(2)	S3 – O31	1.447(2)
S2 – O22	1.448(2)	S3 – O32	1.449(2)
S2 – O23	1.454(2)	S3 – O33	1.464(2)
S2 – S3	2.1376(12)		
Cr1 – O1 – Cr2	96.12(7)	Cr1 – O2 – Cr2	97.81(7)
Cr1 – O11 – S1	132.99(10)	Cr2 – O12 – S1	132.52(10)
O1 – Cr1 – O2	80.35(7)	O1 – Cr2 – O2	80.17(7)
O1 – Cr1 – N20	99.10(8)	O1 – Cr2 – N40	94.78(7)
O1 – Cr1 – N11	175.2(3)	O1 – Cr2 – N31	172.07(14)
O1 – Cr1 – N21	93.69(7)	O1 – Cr2 – N41	94.60(7)
O1 – Cr1 – O11	92.04(7)	O1 – Cr2 – O12	93.84(7)
O2 – Cr1 – N20	90.96(7)	O2 – Cr2 – N40	91.57(7)
O2 – Cr1 – N11	95.19(7)	O2 – Cr2 – N31	94.40(7)
O2 – Cr1 – N21	169.68(7)	O2 – Cr2 – N41	171.50(9)
O2 – Cr1 – O11	94.95(7)	O2 – Cr2 – O12	93.40(7)
N20 – Cr1 – N11	79.4(7)	N40 – Cr2 – N31	79.51(7)
N20 – Cr1 – N21	81.62(8)	N40 – Cr2 – N41	82.13(7)
N20 – Cr1 – O11	168.14(12)	N40 – Cr2 – O12	170.67(11)
N11 – Cr1 – N21	90.45(7)	N31 – Cr2 – N41	90.09(8)
N11 – Cr1 – O11	90.17(7)	N31 – Cr2 – O12	92.23(7)
N21 – Cr1 – O11	93.67(8)	N41 – Cr2 – O12	93.64(7)
C16 – N11 – C12	120.0(2)	C36 – N31 – C32	119.4(2)
N11 – C12 – C13	121.6(2)	N31 – C32 – C33	121.9(2)
C12 – C13 – C14	118.5(2)	C32 – C33 – C34	118.5(2)
C13 – C14 – C15	120.0(2)	C33 – C34 – C35	119.9(2)
C14 – C15 – C16	118.7(2)	C34 – C35 – C36	118.6(2)
C15 – C16 – N11	121.2(2)	C35 – C36 – N31	121.7(2)
C15 – C16 – C17	124.3(2)	C35 – C36 – C37	123.7(2)
N11 – C16 – C17	114.5(2)	N31 – C36 – C37	114.7(2)



C16 - C17 - N20	108.0(2)	C36 - C37 - N40	107.9(2)
C17 - N20 - C27	111.9(2)	C37 - N40 - C47	112.3(2)
N20 - C27 - C26	112.4(2)	N40 - C47 - C46	112.3(2)
C27 - C20 - C25	121.5(2)	C47 - C46 - C45	121.3(2)
C27 - C26 - N21	117.5(2)	C47 - C46 - N41	117.6(2)
C25 - C26 - N21	120.9(2)	C45 - C46 - N41	121.1(2)
C26 - N21 - C22	119.9(2)	C46 - N41 - C42	119.5(2)
N21 - C22 - C23	122.0(2)	N41 - C42 - C43	122.0(2)
C22 - C23 - C24	118.3(2)	C42 - C43 - C44	118.5(2)
C23 - C24 - C25	119.8(2)	C43 - C44 - C45	119.9(2)
C24 - C25 - C26	119.0(2)	C44 - C45 - C46	118.9(2)
O11 - S1 - O14	109.95(10)	O12 - S1 - O13	107.77(10)
O11 - S1 - O12	108.39(9)	O13 - S1 - O14	112.52(10)
O11 - S1 - O13	107.84(10)	O12 - S1 - O14	110.25(10)
S3 - S2 - O23	105.49(8)	S2 - S3 - O33	101.67(8)
S3 - S2 - O22	106.97(8)	S2 - S3 - O32	103.91(8)
S3 - S2 - O21	101.84(8)	S2 - S3 - O31	107.16(8)
O21 - S2 - O23	112.65(10)	O31 - S3 - O33	113.91(11)
O21 - S2 - O22	114.21(10)	O31 - S3 - O32	115.06(10)
O22 - S2 - O23	114.29(11)	O32 - S3 - O33	113.42(10)
<hr/>			
C16 - C17 - N20 - C27	78.9(2)	C36 - C37 - N40 - C47	-78.6(2)
C17 - N20 - C27 - C26	-123.8(2)	C37 - N40 - C47 - C46	124.3(2)
O21 - S2 - S3 - O33	53.9(1)		

nediamine)chromium(III)) ion.<sup>25</sup> The S1-O13 distance, 1.465(2) Å, is slightly longer than the equivalent S1-O14 of 1.442(2) Å. The difference in hydrogen bonds (Table 5) to the oxygen atoms seems to be responsible for this discrepancy.

The Cr-O2 distances are identical <Cr-O2> = 1.935 Å and significantly shorter than the two Cr-O1 bonds which are similar in magnitude, <Cr-O1> = 1.960 Å. The latter distance is comparable with the Cr-O bond lengths normally observed in dinuclear di-μ-hydroxo-chromium complexes.<sup>20,21,25,26,32,37,53</sup> In the related compound μ-carbonato-di-μ-hydroxo-bis(1,4,7-triazacyclononane)-chromium(III) iodide where the cations are on crystallographic mirror planes the two Cr-O distances exhibit similar variations, 1.944(6)

Table 4. Distances (Å) from the least squares plane defined by the atoms marked with \*.

Cr1*	0.151	N11	0.378
Cr2*	0.151	N21	0.146
O1*	-0.148	N31	0.232
O2*	-0.153	N41	0.210
H1	0.26		
H2	0.12		

Å and 1.981(6) Å.<sup>31</sup> The irregularity of the Cr,O1,O2,Cr' bridging system is even more pronounced in this complex. The Cr-Cr distance is 2.898(2) Å and the angle between the two Cr,O1,O2 planes have been calculated to 28° by the present authors.

Table 5. Possible hydrogen bonds (Å) in [(bispicam)Cr(OH)<sub>2</sub>(SO<sub>4</sub>)Cr(bispicam)] S<sub>2</sub>O<sub>6</sub> · 2.8 H<sub>2</sub>O.

D	- H	- A	D - A	D - H - A
O1	- H1	- O4 <sup>a</sup>	2.746(3)	166(4)
O2	- H2	- O13 <sup>b</sup>	2.673(2)	173(4)
N40	- H40	- O21 <sup>c</sup>	2.960(3)	150(3)
O3	- H301	- O14 <sup>d</sup>	2.850(3)	169(4)
O3	- H302	- O33 <sup>e</sup>	2.831(3)	169(4)
O4	- H401	- O3 <sup>f</sup>	2.732(3)	170(4)
O4	- H402	- O13 <sup>d</sup>	2.812(3)	163(4)
O5	-	O31 <sup>g</sup>	3.015(5)	
O6	-	O14 <sup>d</sup>	3.02(2)	
O6	-	O4 <sup>h</sup>	2.83(2)	

a: (1-x, y-½, ½-z)

b: (x, ½-y, ½+z)

c: (1-x, -y, -z)

d: (1-x, ½+y, ½-z)

e: (x, 1+y, 1+z)

f: (x, 1½-y, ½+z)

g: (x, y, 1+z)

h: (x, 1½-y, z-½)

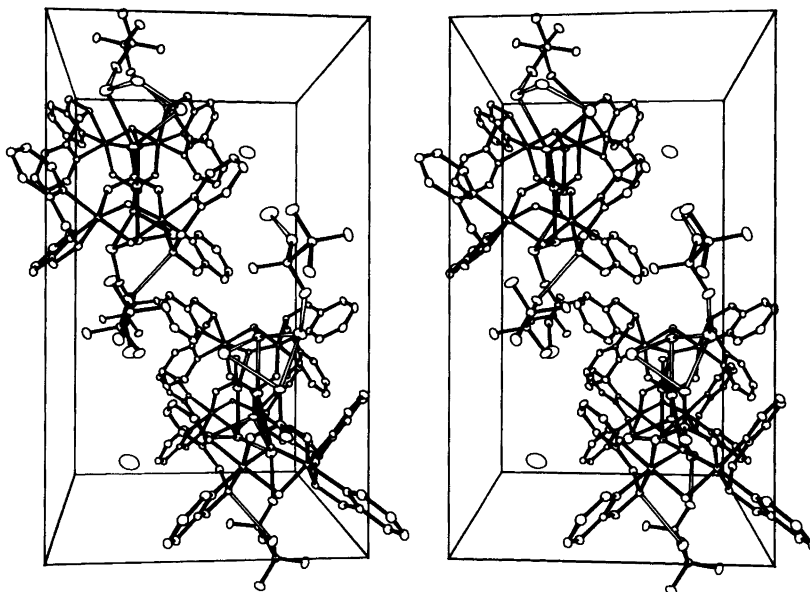


Fig. 5. Stereo pair illustrating the packing viewed along  $c^*$ . The open bonds indicate the possible hydrogen bonds in the structure.

The molecular dimensions of the tridentate bispicam ligand have been compared with those found in the related bidentate and tetradentate ligands. The geometry (bond lengths and angles) of the ligands observed in the different complexes are in good agreement.<sup>32,36,44,54-56</sup>

The conformation of the dithionate ion is approximately staggered, the dihedral angle O21-S2-S3-O33 being  $53.9(1)^\circ$ , which is the energetically favoured conformation often observed in crystal structures containing this ion. The other geometrical features, bond lengths and angles, also agree well with the results from previous structure determinations.<sup>25,32,37,56-58</sup>

A view of the packing in the unit cell is shown in Fig. 5. Table 5 lists the geometrical details for the probable hydrogen bonds which are also indicated on Fig. 5. The dimeric cations are linked by hydrogen bonds from one of the bridging hydroxo groups to one of the coordinating sulfate oxygen atoms. The two fully populated water molecules are both participating in these hydrogen bonds, O3 links the sulfate and the dithionate groups and O4 interacts with two different cations.

The water molecules that correspond to the partly populated positions (O5 and O6) are only

involved in one and two probable hydrogen bonds, respectively. This could explain why these water positions are not fully populated.

#### Electronic Spectra

The electronic spectra of the dimeric compound (vis. region) is shown in Fig. 6a. The intensity of the first absorption band ( $\epsilon = 88$  at 533.3 nm) is remarkably low compared to the intensities of the bands of related compounds with two bridging ligands such as  $\Delta, \Lambda$ -[(en)<sub>2</sub>Cr(OH)(SO<sub>4</sub>)Cr(en)<sub>2</sub>]<sup>3+</sup> ( $\epsilon = 204$ )<sup>24</sup> and [(bispicen)Cr(OH)<sub>2</sub>Cr(bispicen)]<sup>4+</sup> ( $\epsilon = 197$ ).<sup>19</sup> In forthcoming publications we will illustrate that this seems to be a common feature for the spectra of dimeric complexes with bispicam ligands in *cis*-positions to each other while [(OH)(bispicam)Cr(OH)<sub>2</sub>Cr(bispicam)(OH)]<sup>2+</sup> with the amine ligands in *trans*-positions to each other has an absorption band of "normal" intensity ( $\epsilon = 240$ ).

The electronic spectrum of the trimeric chromium compound (vis. region) is shown in Fig. 6b. The spectrum is independent of pH in the region  $6.5 \leq \text{pH} \leq 1$  indicating that a structure with a terminal hydroxo group is unlikely.

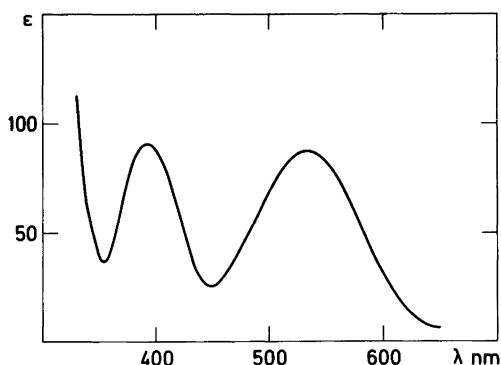


Fig. 6a. The absorption spectrum (visible region) of [(bispicam)Cr(OH)<sub>2</sub>(SO<sub>4</sub>)Cr(bispicam)]<sup>2+</sup>.

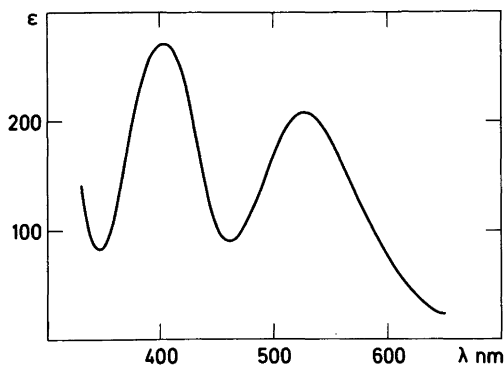


Fig. 6b. The absorption spectrum (visible region) of [Cr<sub>3</sub>(bispicam)<sub>3</sub>(OH)<sub>4</sub>(SO<sub>4</sub>)]<sup>3+</sup>.

### Magnetic Properties

The average magnetic susceptibility and the effective magnetic moment as functions of temperature of the title compound are shown in Fig. 7. The susceptibility data were fitted to the expression

$$\chi'(T) = - \frac{N \sum_i \left( \frac{\partial E_i}{\partial H} \right) \exp(-E_i/kT)}{H \sum_i \exp(-E_i/kT)} \frac{1}{2} + \frac{C}{T} + K \quad (1)$$

by minimization of

$$\sum_j \frac{[\chi_{\text{obs}}(T_j) - \chi'(T_j)]^2}{\sigma^2(\chi(T_j)) + \left( \frac{\partial \chi_{\text{obs}}}{\partial T}(T_j) \right)^2 \sigma^2(T_j)} \quad (2)$$

Here,  $\chi_{\text{obs}}$  is the experimental molar susceptibility per chromium atom corrected for diamagnetic contributions. The  $E_i$  in (1) are the energies of the components of the ground state manifold of the complex as obtained, for instance, by the Heisenberg-type model Hamiltonian

$$\mathcal{H} = J\hat{S}_1 \cdot \hat{S}_2 - j(\hat{S}_1 \cdot \hat{S}_2)^2 + \mu_B g H \cdot \hat{S} \quad (3)$$

in which the triplet, quintet and septet energies are  $J + 6.5j$ ,  $3J + 13.5j$  and  $6J + 9.0j$ , respectively, neglecting the Zeeman term in (3). In the following, (3) is referred to as model 2. A spe-

cialized case of (3) where the parameter  $j$  is fixed to zero is referred to as model 1. An entirely generalized Hamiltonian has the eigenvalues  $E(S') + g\mu_B H M_S$ , where  $S' (= S_1 + S_2)$  can have the values 0–3 in this case of two  $S = 3/2$  centers. In this so-called model 3 the triplet, quintet and septet energies,  $E(1)$ ,  $E(2)$  and  $E(3)$ , respectively, are independent parameters. All of the three models neglect zero-field splittings and assume an isotropic Zeeman effect.  $C$  in (1) is a parameter accounting for small amounts of impurities showing Curie-law behaviour, monomeric species, for example.  $K$  in (1) represents a temperature independent susceptibility apart from the sum of the Pascal constants. The estimated standard deviations used in (2) are reported elsewhere.<sup>23</sup>

The results of the data fittings are shown in Table 6. It is apparent that the observed susceptibility data are only poorly described by models 1 and 2, the variance per degree of freedom,  $\text{var}/f$ , being 31.8 and 2.82, respectively. According to model 1  $g$  is even fitted to the unrealistic value of 2.024(4), and the amounts of monomeric impurity are in both cases calculated to be negative. Only model 3 fits the data from a statistical point of view.  $(\text{var}_2/f_2)/(\text{var}_3/f_3) = 2.41$  which is beyond the 99.95 fractile of the  $V^2$  distribution. According to  $V^2_{0.9995}(365,364)$  model 3 is thus significantly<sup>59</sup> better than model 2 and leads to the triplet, quintet and septet energies of 14.4(1)  $\text{cm}^{-1}$ , 27.0(1)  $\text{cm}^{-1}$  and 46.5(2)  $\text{cm}^{-1}$ , respectively. The energy ratios are close to 1:2:3 and far from 1:3:6 according to the simple Heisenberg Hamil-

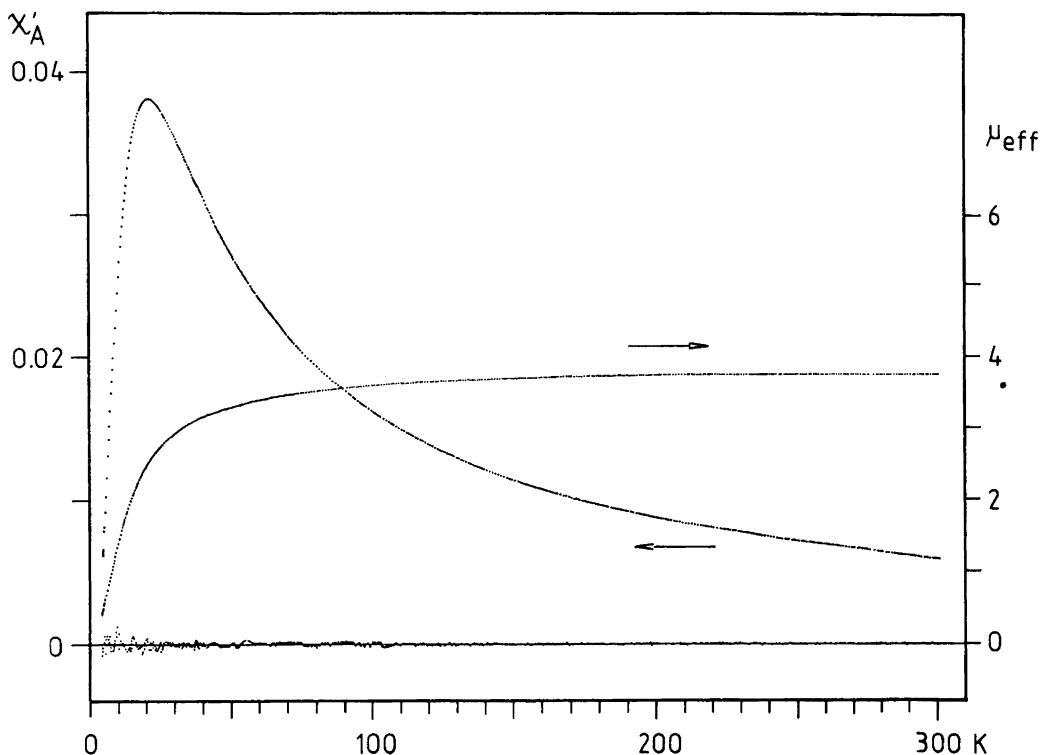


Fig. 7. Magnetic susceptibility per chromium (left scale, cgsu) and effective magnetic moment (right scale,  $\mu_B$ ) of  $[(\text{bispicam})\text{Cr}(\text{OH})_2(\text{SO}_4)\text{Cr}(\text{bispicam})]\text{S}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$ . The lower and almost random distribution of dots around the abscissa indicates  $50(\chi_{\text{obs}} - \chi_{\text{calcd}})$ , where  $\chi_{\text{calcd}}$  is obtained from the parameters of model 3 in Table 6.

Table 6. Parameters Derived from Magnetic Susceptibility Data.<sup>a</sup>

parameter	model 1	model 2	model 3
$J$ , $\text{cm}^{-1}$	7.30(4)	5.72(3)	—
$j$ , $\text{cm}^{-1}$	—	-0.82(1)	—
$E(1)$ , $\text{cm}^{-1}$	7.30(4) <sup>b</sup>	11.05(9) <sup>b</sup>	14.4(1)
$E(2)$ , $\text{cm}^{-1}$	21.9(1) <sup>b</sup>	28.2(3) <sup>b</sup>	27.0(1)
$E(3)$ , $\text{cm}^{-1}$	43.8(2) <sup>b</sup>	41.7(6) <sup>b</sup>	46.5(2)
$g$	2.024(4)	1.963(1)	1.983(1)
$f^c$	366	365	364
$\text{var}/f^d$	31.8	2.82	1.17 <sup>e</sup>
% monomer	-0.022(4)	-0.09(5)	0.083(5)

<sup>a</sup>See text for description of the three models.

<sup>b</sup>Calculated from the derived parameter(s) for comparison with results from other models. <sup>c</sup>The number of degrees of freedom in the calculation; this is simply the number of data (370) minus the number of variables. <sup>d</sup>Variance/degree of freedom. <sup>e</sup>No correlation coefficient exceeded 0.85.

tonian in model 1. The discrepancy is far bigger than previously observed by us in chromium(III) dimers.

Magnetic data were collected for two independent samples of the dithionate salt having identical X-ray Guinier diagrams. The results were identical within the experimental uncertainty. Similar measurements and fitting procedures have been performed for perchlorate and iodide salts. Two different perchlorate samples showed triplet energies,  $E(1)$ , 5.91  $\text{cm}^{-1}$  and 7.18  $\text{cm}^{-1}$ . The iodide salt had  $E(1) = 12.04 \text{ cm}^{-1}$ .

The results for the dithionate salt for which the crystallographic information is presented herein can be compared with those previously obtained for other dimeric chromium(III) species with two bridging hydroxy groups.<sup>39,60</sup> The direct effect of the bridging sulfato group on the magnetic exchange interaction is expected to be very small since this is governed by orbital overlaps of the

$\pi$ -type between the metal centers.<sup>39</sup> Therefore, the main interaction is expected to occur via the  $\mu$ -hydroxo groups as in genuine di- $\mu$ -hydroxo complexes. As seen from Fig. 4 there is an obvious indirect effect of the  $\mu$ -sulfato group. The arrangement of Cr1, Cr2, O1 and O2 is forced to deviate significantly from planarity, the angle between the planes Cr1,O1,O2 and Cr2,O1,O2 being 23°. This could have an effect on the  $\pi$ -overlap via O1 and O2. A lengthy calculation by application of the angular overlap model showed, however, that also this effect is quite small. The details will not be given here but the results make sense since the gain in  $\pi$ -overlap above the Cr<sub>2</sub>O<sub>2</sub>-system (referring to Fig. 4) due to the bending of this arrangement is more or less compensated by a loss in  $\pi$ -overlap below this system.

From a magnetic point of view the present system is, therefore, related to the di- $\mu$ -hydroxo systems. In order to correlate the magnetic exchange parameters with the structural results we have used the Glerup-Hodgson-Pedersen (GHP) model,<sup>39</sup> average Cr1-O-Cr2 angles of  $\varphi = 99.74(7)^\circ$  and average Cr-O distances of  $r = 1.945(2) \text{ \AA}$ . As the angles describing the positions of the hydrogen atoms in the bridging system, previously referred<sup>39</sup> to as out-of-plane angles  $\theta$ , we here use the angles between the O-H vectors and the O1-O2 vector. These angles O1-H1,O1-O2: 48(3)° and O2-H2,O1-O2: 36(3)° with an average of 42, and we substitute this value for  $\theta$  as rationalized in terms of the angular overlap model as discussed above. Using estimated standard deviations as previously discussed and the above values for  $r$ ,  $\varphi$  and  $\theta$  we calculate a singlet-triplet splitting in terms of competing antiferro- and ferromagnetic contributions  $J = J_{af} - J_f = 15(3) \text{ cm}^{-1}$ . This result differs far less than one standard deviation from  $E(1)$  according to model 3.

The reason for the shortcoming of the Heisenberg-Hamiltonian for this complex is not yet entirely clear. According to the GHP model<sup>39</sup> this Hamiltonian is valid only in the limiting case where the splittings between different spin multiplets of the excited charge-transfer configurations are small compared with their excitation energies. This assumption may be less realistic in the present case than in the genuine di- $\mu$ -hydroxo complexes where the metal centers are approximately 0.1 Å further apart and, consequently,

direct metal-metal interelectronic repulsion expected to be much smaller. We are presently attempting to incorporate these considerations in the GHP model.

Obvious targets for comparison would be salts of the tri- $\mu$ -hydroxo-bis[1,4,7-trimethyl-1,4,7-triazacyclononanechromium(III)] ion where the metal centers are even closer together, viz. 2.642–2.664 Å.<sup>31,61,62</sup> Due to their strong exchange interactions only triplet energies (140–160 cm<sup>-1</sup>) have been estimated with reasonable accuracy.

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