The Structure of *cis*-Aquahydroxobis (2-pyridylmethylamine)-chromium(III) Dithionate Studied by X-Ray Diffraction and Spectroscopic Methods

SINE LARSEN, KURT B. NIELSEN and IB TRABJERG

Chemical Laboratory IV, H.C. Ørsted Institute, Universitetsparken 5, DK-2100 København Ø, Denmark

The crystal structure of the title compound has been determined by X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/c$, $Z=4$ with unit cell dimensions $a = 10.210$ Å, $b=10.680$ Å, $c=16.992$ Å and $\beta=101.25°$. The structure was solved and refined from diffractometer data to a final R-value of 0.046. The complex cation has the pyridine nitrogen atoms in a *trans* configuration and the other ligators in *cis* configurations. The Cr–O(hydroxo) bond is considerably shorter than the Cr–O (water) bond 1.93 Å *vs.* 2.00 Å. The pyridine rings of the ligands are almost perpendicular.

The polarized single crystal spectra recorded with the E-vector in the *a–b* plane, have the sharpest absorption maxima when E is parallel to the *a*-axis. Emission and exitation spectra measured on powdered samples show spin-forbidden transitions at 640 and 708 nm. At 1.7 K the observed lifetime was 28μs. The strong-field parameters obtained from the spectra are 10 $Dq=1900$ cm^{-1}, $B=500$ cm^{-1} and $C=3450$ cm.$^{-1}$

A number of different complexes of chromium(III) and cobalt(III) with 2-pyridylmethylamine as ligand have been prepared and characterized by their solution spectra by Kirsten Michelsen.[1-5] If we consider the octahedral complexes with two molecules of 2-pyridylmethylamine as ligands, several isomers are possible due to the difference between the two ligating nitrogen atoms in the bidentate ligand. For the complexes corresponding to a *cis* arrangement of the unidentate ligands three different geometrical isomers may exist. They are named by consider-ing firstly the spatial arrangement of the unidentate ligands, then the arrangement of the pyridine nitrogen atoms and finally the arrangement of the methylamine nitrogen atoms. According to this nomenclature the three geometrical isomers can be classified as a *cis,trans,cis*, a *cis,cis,trans*, and a *cis,cis,cis* isomer. Kirsten Michelsen was able to isolate two series of complexes, called α and β.[2,3] From spectroscopic measurements she concluded that the α-series corresponds to either the *cis, trans,cis* or to the *cis,cis,trans* isomers, and the β-series to the *cis,cis,cis* isomers.

The compound studied in this work is of the α-series assuming equivalence between the hydroxyl group and the water molecule. The structure analysis was undertaken to establish the configuration of the α-series complexes and to obtain information about the overall symmetry and the structure of a *cis*-aqua hydroxo chromium(III) complex since no structural data is available for this particular type of compound. The electronic structure of the complex is elucidated by measurements of crystal spectra in the ligand field range.

EXPERIMENTAL

Chrystallographic examination. A sample of the title compound was kindly provided by Kirsten Michelsen. It crystallizes as bright red plates. Preliminary Weissenberg and precession photographs showed that the crystals are mono-clinic, the space group is uniquely determined to be $P2_1/c$ from the systematically absent reflec-

tions. The density was measured by flotation in a mixture of bromobenzene and 1,2-dibromo-ethane.

A single crystal with dimensions $0.3 \times 0.1 \times 0.03$ mm³ was chosen for the data collection and for the determination of unit cell parameters on a Picker FACS-1 diffractometer. The measurements were performed at 22 °C using graphite monochromated-Mo$K\alpha$ radiation. The data were obtained by operating the diffractometer in the $\theta - 2\theta$ scan mode at a rate of $1°\text{min}^{-1}$ in 2θ. The reflections were collected in the hemisphere ($h \leq 0$) which had $2.4° \leq 2\theta \leq 42°$. The symmetrical scan range was increased with 2θ following the expression $\Delta 2\theta_{sc} = 2.4° + 2 \times 0.346 \tan \theta$. Background counts were made at each end of the scan range for 20 s.

The intensities for 6 standard reflections recorded after every 60 reflections showed that no deterioration or misalignment had occured during the data collection. The data were corrected for Lorentz and polarization effects and the symmetry related reflections were averaged. Of the 1900 independent reflections so obtained 1329 satisfied the inequality $|F|^2 \geq 2\sigma(|F|^2)$, and these were used for the structure solution and refinement.

The following computer programs were employed during the computations: the Vanderbilt system[6] for diffractometer operations, a data reduction program of local origin, ORTEP II[7] for the illustrations, the XRAY[8] system for the crystal structure analysis and Simplex[9] for the weight analysis.

Using the values for the uncharged atoms the scattering factors used in the calculations were taken from Cromer and Mann[10] except for H were the results from Stewart et al.[11] were used. The anomalous dispersion corrections added to the scattering factors of chromium and sulfur were calculated by Cromer and Liberman.[12]

Spectroscopic examination. The electronic structure was investigated by recording the single crystal polarized absorption spectra and both emission and excitation spectra of powdered samples.

The largest available crystals with a surface of approximately 0.25×0.5 mm² were used for the measurements of the polarized absorption spectra. The crystal surface is parallel to the $a-b$ plane elongated along the b-axis.

The absorption spectra were recorded at room temperature and at 80K on a 2m Jena QI-spectrograph and a Cary 14 spectrometer. The emission spectra were detected by a Jarrell Ash ½ m Ebert scanning monochromator type JE 82–000 equipped with an EMI S-20 cathode

photomultiplier. The excitation for the DC-measurements was made by use of a Varian Lamp type VIX 300 and filtered by a MacPherson 0.3 m scanning monochromator, Model 218.

The lifetime measurements were performed by excitation with a dye laser pumped by an nitrogen laser AVCO 530. A methanol solution 0.01 M in β-methylumbelliferrone and 1.5 M in HClO₄ was used as the dye.

DC-signals were amplified by a Keithly nA meter and AC-signals by a Tektronix type 454 oscilloscope with a signal output and a PAR-boxcar integrator, model 160, before they were recorded on a strip-chart recorder.

The spectra obtained from the powdered samples were made by gluing the powder to a copper-plate with Aquadag and mounting the plate in a helium cryostat. The bubbles in the liquid helium were removed by pumping the gasous helium away until the temperature was below the λ-point.

CRYSTAL DATA

cis-Aquahydroxobis(2-pyridylmethylamine)-chromium(III) dithionate. $C_{12}H_{19}N_4O_8S_2Cr$; $M = 463.4$. Monoclinic $a = 10.210(3)$ Å, $b = 10.680(4)$ Å, $c = 16.992(6)$ Å, $\beta = 101.25(2)°$; $V = 1817.2$ Å³; $d_{obs} = 1.69$ g/cm³; $Z = 4$; $d_{cal} = 1.694$ g/cm³. $\mu(\text{Mo}K\alpha) = 8.71$ cm⁻¹. $F(000) = 996$. Systematically absent reflections: $h0l$ when l odd, $0k0$ when k odd; space group $P2_1/c$ (C_{2h}^5 No.14). The plate face is $\{001\}$.

DETERMINATION AND REFINEMENT

The positions for the chromium atom and the two sulfur atoms were determined from the Patterson function. The remaining non-hydrogen atoms were located by Fourier syntheses. The structure was refined by the method of least squares minimizing $\Sigma w ||F_o| - |F_c||^2$. Due to the limited resolution of the diffraction data anisotropic thermal parameters were only introduced if a difference Fourier and Hamilton's R-value test indicated that they provided a better description of the thermal motion. Using this criterium anisotropic temperature factors were gradually introduced to all the heavier atoms. After a unit weighted refinement, a difference Fourier map showed clearly the positions for the hydrogen atoms of the 2-pyridylmethylamine ligands. The hydrogen atoms of the hydroxo group and the water molecule were found in areas with more

Table 1. Final fractional coordinates and equivalent isotropic temperature factors, U_{eq}, in units of $Å^2 \times 10^{-2}$.

Atom	x	y	z	$U_{eq}{}^a$
The cation:				
Cr	0.64812(10)	0.37121(10)	0.24079(6)	2.11(6)
O1	0.5281(4)	0.2397(4)	0.2585(2)	2.4(3)
O2	0.5066(4)	0.4998(4)	0.2426(3)	3.1(3)
N11	0.7310(5)	0.3886(5)	0.3612(3)	2.7(4)
C15	0.6960(9)	0.4738(7)	0.4110(5)	5.3(6)
C14	0.7607(10)	0.4526(8)	0.4894(5)	6.7(7)
C13	0.8616(10)	0.4013(9)	0.5180(4)	6.1(7)
C12	0.8983(8)	0.3145(7)	0.4684(5)	4.4(5)
C11	0.8314(7)	0.3070(6)	0.3898(4)	2.8(5)
C16	0.8587(7)	0.2119(6)	0.3322(4)	3.5(5)
N12	0.7977(5)	0.2407(5)	0.2479(3)	2.5(4)
N21	0.6048(5)	0.3575(5)	0.1173(3)	2.3(4)
C25	0.5043(7)	0.2895(7)	0.0747(5)	3.7(5)
C24	0.4846(8)	0.2811(7)	−0.0075(5)	4.8(6)
C23	0.5652(9)	0.3471(8)	−0.0479(4)	4.6(6)
C22	0.6660(7)	0.4197(6)	−0.0051(4)	3.6(6)
C21	0.6840(7)	0.4229(6)	0.0778(4)	2.7(5)
C26	0.7928(7)	0.4969(6)	0.1267(4)	3.6(5)
N22	0.7765(5)	0.5078(5)	0.2109(3)	2.6(4)
The Dithionate Ion				
S1	0.1727(2)	0.3917(2)	0.29334(11)	2.96(11)
S2	0.1491(2)	0.3146(2)	0.17533(11)	3.03(12)
O11	0.2848(4)	0.4778(4)	0.3016(3)	4.1(3)
O12	0.0494(4)	0.4556(5)	0.2946(3)	5.0(4)
O13	0.1991(5)	0.2867(4)	0.3470(3)	5.6(4)
O21	0.2619(5)	0.2320(5)	0.1807(3)	5.2(4)
O22	0.0250(5)	0.2492(5)	0.1665(3)	5.6(4)
O23	0.1491(6)	0.4169(5)	0.1218(3)	7.0(4)

$^a U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

diffuse density. Due to the limited resolution of the diffraction data the contributions from the hydrogen atoms were included but their parameters were not refined. Their positional parameters were fixed at idealized values, the thermal parameters were given the value of the refined isotropic temperature factor of the atom to which it is bonded. The weights[9] used in the final cycles of least squares refinement follow the expression: $w^{-1} = 0.32 + 0.53\sigma^2(F) - 0.0036|F| + 0.0003F^2$.

In the last cycle of least squares the maximum shift of parameters was 0.24σ and the unit weighted and weighted residual defined as

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}, \quad R_w = \left\{ \frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2} \right\}^{1/2}$$

had decreased to 0.046 and 0.031, respectively. The goodness of fit, $G = \{\Sigma_w \Delta F^2/(n-m)\}^{1/2}$ where n and m represent the number of reflections and variables is 0.93.

The final parameters are given in Table 1. The parameters in the refinement for the hydrogen atoms, the anisotropic thermal parameters and a list of observed and calculated structure amplitudes may be obtained from the authors.

STRUCTURE

The bond lengths and bond angles for the two ions are given in Table 2 and the stereo chemistry and atomic labelling are illustrated by Figs. 1 and 2. The conformation of the dithionate ion is
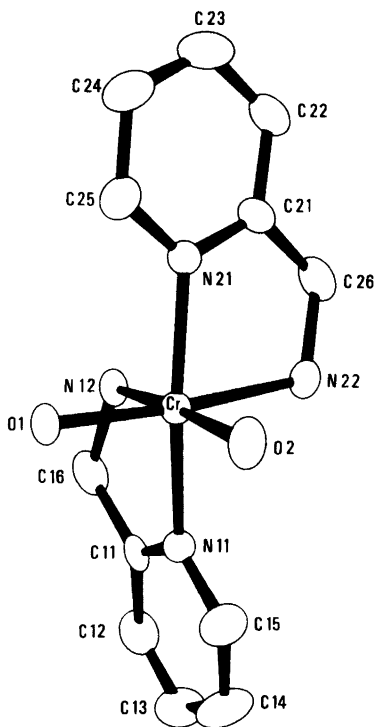
Fig. 1. An ORTEP drawing of *cis*-aquahydroxo-bis-(2-pyridylmethylamine)chromium(III)   ion showing the atomic labelling.
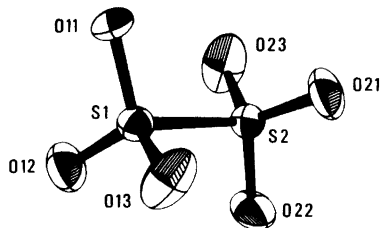

Fig. 2. An ORTEP drawing of the dithionate ion.

approximately staggered, the dihedral angle O13–S1–S2–O23 being −168,8(4)°. The S1–S2 bond length is 2.137 Å and none of the S–O bonds differ significantly from their mean, <S–O>=1.436 Å. All these features are in agreement with those previously obtained in other crystal structure determinations for dithionate containing compounds.[14-19]

The ORTEP drawing of the complex cation shown in Fig. 2 illustrates the spatial arrangement around the chromium atom. The oxygen atoms are *cis*, the pyridine nitrogens are *trans* and the amino nitrogens are *cis*. Thus this compound, which is an example of a type of complexes which Kirsten Michelsen earlier classified as α-isomers, has a *cis,trans,cis* configuration.

As was observed earlier in the structure determination for the di-μ-hydroxobis[bis{ (*S*)-1-(2-pyridyl)ethylamine}] chromium(III) ion[17] there
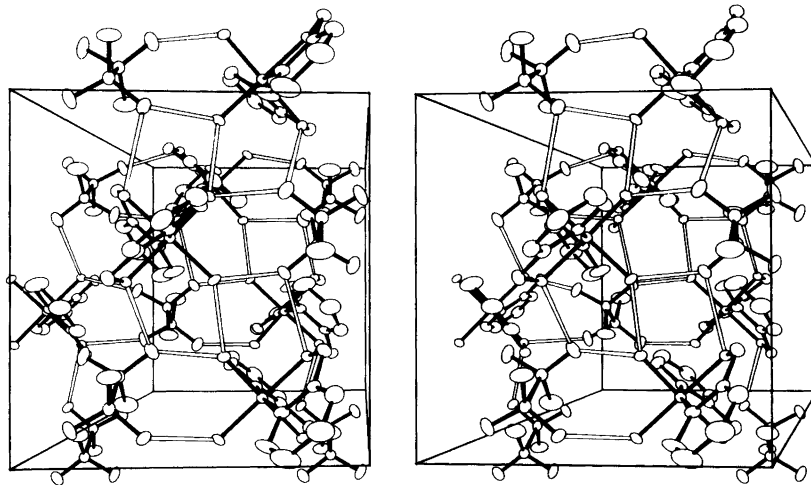

Fig. 3. Stereo pair of the packing viewed along the *c** axis perpendicular to the plate face of the crystals.

Table 2. Bond lengths (Å) and selected bond angles (°) with e.s.d.'s.

Cation

Cr–O1	1.926(4)	Cr–O2	1.998(5)
Cr–N11	2.065(5)	Cr–N21	2.063(5)
Cr–N12	2.054(5)	Cr–N22	2.089(5)
N11–C11	1.360(9)	N21–C21	1.343(9)
C11–C12	1.378(10)	C21–C22	1.385(10)
C12–C13	1.354(12)	C22–C23	1.378(10)
C13–C14	1.363(13)	C23–C24	1.365(13)
C14–C15	1.369(11)	C24–C25	1.374(11)
C15–N11	1.338(10)	C25–N21	1.347(9)
C11–C16	1.475(10)	C21–C26	1.479(9)
C16–N12	1.479(9)	C26–N22	1.476(10)
O1–Cr–O2	90.8(2)	N12–Cr–N22	89.6(2)
O1–Cr–N11	93.5(2)	O1–Cr–N21	95.2(2)
O2–Cr–N11	94.6(2)	O2–Cr–N21	93.0(20)
O1–Cr–N12	89.1(2)	O2–Cr–N22	90.8(2)
N11–Cr–N12	81.2(2)	N21–Cr–N22	79.8(2)
C11–N11–C15	119.0(6)	C21–N21–C25	118.8(6)
N11–C11–C12	120.4(7)	N21–C21–C22	121.5(6)
N11–C11–C16	115.5(6)	N21–C21–C26	117.2(6)
C12–C11–C16	124.1(6)	C22–C21–C26	121.4(7)
C11–C12–C13	119.8(7)	C21–C22–C23	119.2(7)
C12–C13–C14	119.7(7)	C22–C23–C24	119.2(7)
C13–C14–C15	119.4(8)	C23–C24–C25	119.6(7)
C14–C15–N11	121.6(7)	C24–C25–N21	121.8(7)
C11–C16–C12	113.7(5)	C21–C26–N22	111.9(6)
C16–N12–Cr	111.5(4)	N26–N22–Cr	112.0(4)

Anion

S1–S2	2.137(3)	O11–S1–S2	106.1(2)	O21–S2–S1	103.5(2)
S1–O11	1.454(5)	O12–S1–S2	105.0(2)	O22–S2–S1	102.8(2)
S1–O13	1.436(5)	O13–S1–S2	105.5(2)	O23–S2–S1	106.9(2)
S1–O13	1.437(5)	O11–S1–O12	111.9(3)	O21–S2–O22	112.9(3)
S2–O21	1.439(5)	O11–S1–O13	112.7(3)	O21–S2–O23	114.4(4)
S2–O22	1.430(5)	O12–S1–O13	114.7(3)	O22–S2–O23	114.8(3)
S2–O23	1.422(6)				

Table 3. Hydrogen bond distances in Å. The acceptor hydrogen distances are from 1.60–2.30 Å. ∠A–H–D~140–180°.

Donor	Acceptor	
O1	O21	2.782(6)
O2	O11	2.659(7)
O2	O1^a	2.586(6)
N12	O22^b	2.925(8)
N12	O11^c	3.004(7)
N22	O12^b	2.925(7)
N22	O21^a	3.092(7)

^{a}1–*x*, ½+*y*, ½–*z*. ^{b}1+*x*, *y*, *z*. ^{c}1–*x*, *y*–½, ½–*z*.

are no differences between the Cr–N(pyridine) and Cr–N(amine) distances. The four independent Cr–N bond lengths are alike and their average value 2.068 Å is in agreement with the Cr–N distances found in related chromium(III) complexes with bidentate ligands.[18-21] The two Cr–O distances are so significantly different that one would expect that the shortest Cr–O1, 1.926(4) Å corresponds to Cr–O(hydroxo) and the longest Cr–O2, 1.998(5) Å to Cr–O(aqua). These values agree well with the bond lengths observed in other chromium(III) hydroxo or aqua complexes.[18-24] Therefore even without any knowledge about the hydrogen positions O1 can
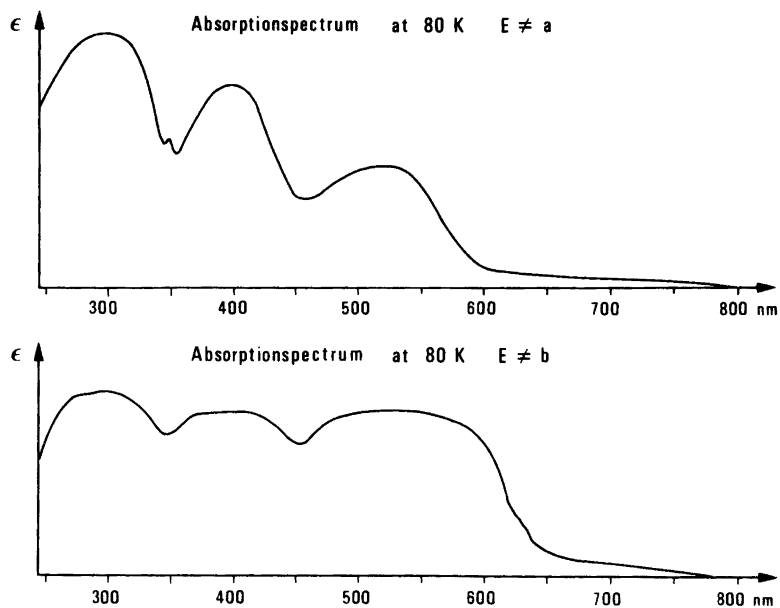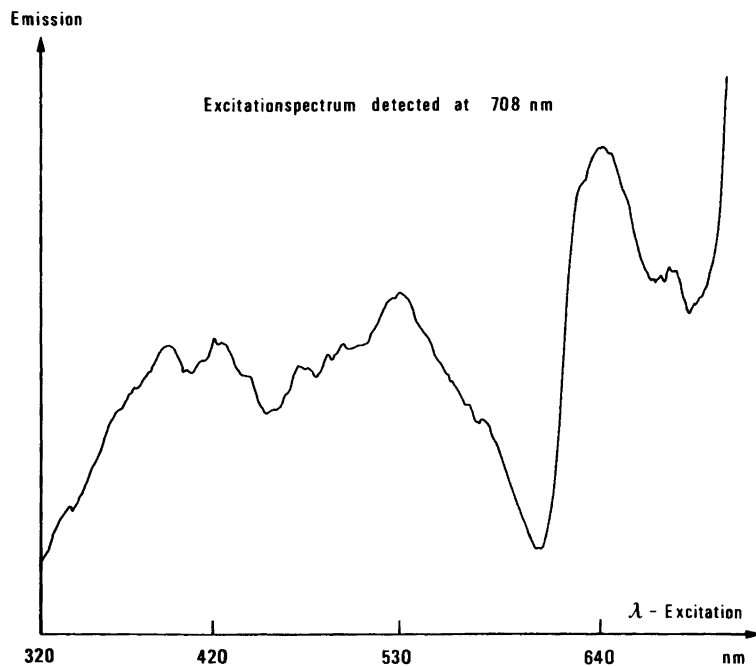
Fig. 4. Polarized absorption spectra at 80 K.

Fig. 5. Uncompensated excitation spectrum recorded at 1.7 K.

be classified as the hydroxo oxygen and O2 as the aqua oxygen.

The calculation of least squares planes showed that the two pyridine rings do not deviate significantly from planarity. The pyridine rings are almost perpendicular. The angle between the
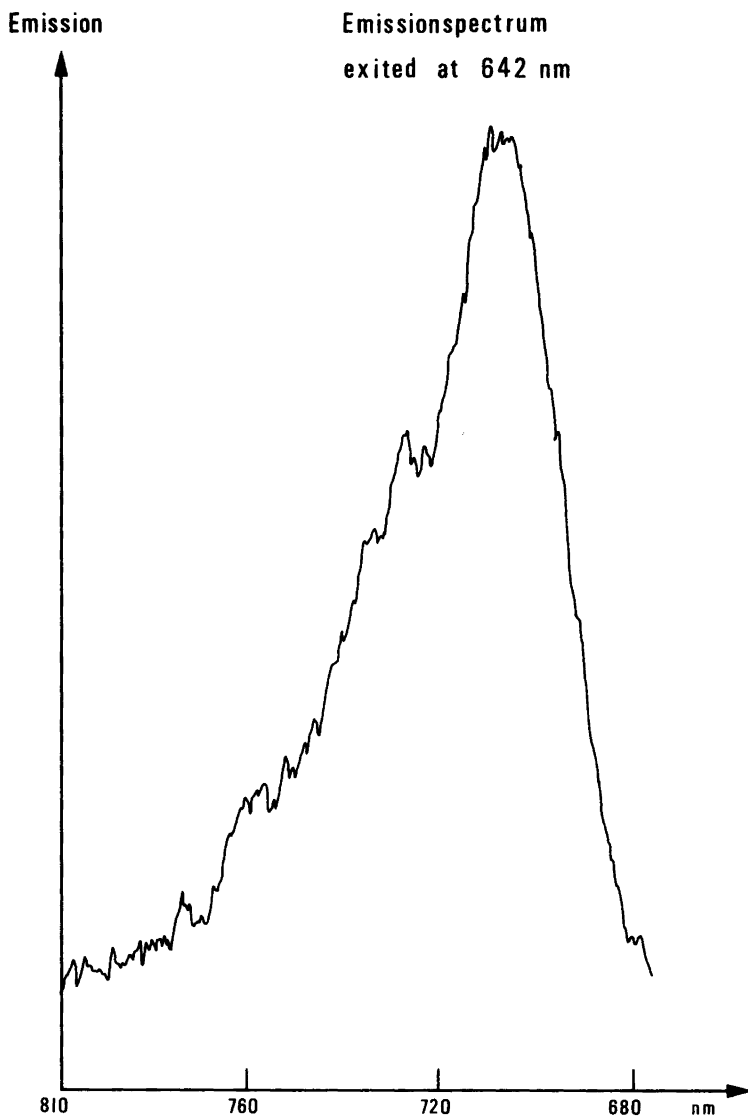
Emission

Emissionspectrum
exited at 642 nm

Fig. 6. Emission spectrum recorded at 1.7 K.

least squares planes is 86°.

The two bidentate ligands take opposite conformations, the dihedral angles N11–C11–C16–N12 and N21–C21–C26–N22 are 15.1(9) and −12.7(8)°, respectively, corresponding to a $\delta\lambda$ conformation. The molecular dimensions of the two chelate ligands are internally in good agreement and consistent with the values found in other octahedral complexes with this ligand and the related ligand 2-pyridylethylamine.[18,25-26]

The packing of the crystal illustrated by the stereo pair in Fig. 3 is mainly determined by hydrogen bonding. Table 3 lists the hydrogen bonds, which are formed from all the possible donor hydrogen atoms. The hydrogen bond between the dithionate ion and the complex cation is almost parallel to the *a*-axis resulting in a chain of alternating dithionate and complex ions. The complex ions related by the two-fold screw axis are linked together by a short hydrogen bond

between the water molecule of one molecule to the hydroxo group of the adjacent. This extensive net of hydrogen bonds formed in the directions of the a and b axis explains why the crystals formed are plates and the plate face is {001}.

ELECTRONIC SPECTRA

Even the largest samples were very small for spectroscopic work, and the absorption spectra could therefore be recorded only with the light propagating along the normal of the plate face. As the molecules are oriented in the crystal with the O1–O2 vector almost parallel to the b axis in this plane, crystal spectra could be obtained with the electric polarization vector at all directions within the {001} plane. Several such spectra were recorded at room temperature. By comparing these two and two, it was observed, that the C_{2v} site symmetry with the 2 symmetry axis in the a-direction gave the best fit. This is consistent with the symmetry derived from the structure, when only the ligating atoms are assumed.

The absorption spectra recorded at 80 K for the two polarisations parallel to the a and b axis are shown in Fig. 4. Three broad maxima are seen in both polarizations, but those measured with the polarization parallel to the b axis are broader than the similar bands with polarization along the a axis. Additionally the maximum with the lowest energy is shifted from 550 to 520 nm going from $E\neq b$ to $E\neq a$. The other peaks are centered around 300 and 400 nm in both polarizations. We assign the peaks at 550 and 520 nm to the $^4A_2\rightarrow{}^4T_2$ transition (O_h-term symbols), the 520 nm being less broad, as the transition to the $^4A_1$ component in C_{2v} symmetry is forbidden. the tops at 400 nm are assigned to the $^4A_2\rightarrow{}^4T_1$ transition, and the 300 nm to a charge transfer band.

The emission and excitation spectra were recorded for powdered samples only. An uncompensated excitation spectrum on powder is shown in Fig. 5. Due to the weak emission the spectrum is noisy so that only the gross outlines should be used. Like the absorption spectrum the excitation spectrum contains two broad bands at 400 and 530 nm, providing evidence that the emission stems from the chromium and not from impurities. The excitation spectrum has a maximum at 640 nm which is not observed in the absorption.

A peak at 708 nm in the emission spectrum is shown in Fig. 6. The 640 nm top is assigned to the $^4A_2\rightarrow{}^2T_1$, and that at 708 nm to the $^4A_2\rightarrow{}^2E$ -spin-forbidden transitions.

From the above assignments, the following ligand field parameters were obtained:

10 $Dq=1900$ cm^{-1}; $B=500$ cm^{-1} and $C=3450$ cm^{-1}.

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