result of decreasing stability of the octahedral structure with decreasing cation size, with a consequent tendency to form fivefold and, finally, tetrahedral coordination. In the alkali metal niobates (Megaw, 1968*b*) cations are displaced by as much as 0·26 Å. These mechanisms may also be contributing to the distortion of the UF_6 octahedron.

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The Crystal and Molecular Structure of Di-μ-hydroxobis[di(1,10-phenanthroline)chromium(III)] Chloride Hexahydrate

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The crystal and molecular structure of di-μ-hydroxobis[di(1,10-phenanthroline)chromium(III)] chloride hexahydrate, $[Cr(phen)_2OH]_2Cl_4.6H_2O$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the triclinic space group $P\bar{1}$ with two dimeric formula units in a cell whose dimensions are $a=14·056$ (7), $b=11·296$ (6), $c=18·990$ (9) Å, $\alpha=87·15$ (3), $\beta=107·63$ (2), and $\gamma=74·68$ (3)°. The observed and calculated densities are 1·39 (4) and 1·342 g cm^{-3} respectively. The structure has been refined by full-matrix least-squares techniques to a conventional R value of 0·077 for 3392 independent intensities greater than three times their estimated standard deviations. The complex consists of pairs of chromium atoms which are linked by two hydroxo bridges, with two 1,10-phenanthroline groups coordinated to each metal; the coordination geometry around each chromium is roughly octahedral. The average Cr–N and Cr–O bond lengths are 2·052 (6) and 1·927 (6) Å respectively, while the Cr–Cr separation is 3·008 (3) Å and the average Cr–O–Cr angle is 102·7 (4)°. The geometry of this complex is compared with that of $[Cr(gly)_2OH]_2$ and with those of complexes of the type $[CuLOH]_2^{n+}$, and the magnetic properties of the complex are discussed in terms of the bridging geometry.

Introduction

We have recently been interested in attempting to correlate the structural and magnetic properties of magnetically condensed copper(II) and chromium(III) systems, with especial emphasis on hydroxo- and halogen-bridged dimeric species (Hodgson, Hale & Hatfield, 1971; Meyer, Singh, Hatfield & Hodgson, 1972; Hodgson, Veal, Hatfield, Jeter & Hempel, 1972). From our magnetic and structural investigations of the complex $[Cu(EAEP)OH]_2^{2+}$, where EAEP is the bidentate ligand 2-(2-ethylaminoethyl)pyridine (Lewis, Hatfield & Hodgson, 1972; Jeter, Lewis, Hempel, Hodgson & Hatfield, 1972) and similar studies on the analogous systems $[Cu(bipy)OH]_2^{2+}$, where bipy is 2,2′-bipyridine (Casey, Hoskins & Whillans, 1970; Majeste & Meyers, 1970; Barnes, Hodgson & Hatfield, 1972) and $[Cu(tmen)OH]_2^{2+}$, where tmen = tetramethylethylenediamine (Mitchell, Bernard & Wasson, 1970; Cole & Brumage, 1970) we were able to deduce that the value of $2J$, the singlet–triplet energy separation, decreases as the Cu–O–Cu bridging angle φ increases, and that $2J$ changes from positive to negative in the region 97 to 99° (Lewis *et al.*, 1972).

We have recently extended these studies to chromium(III) complexes of the type $[CrL_2(OH)]_2^{n+}$, where L is a bidentate ligand, and recently reported the structural and magnetic characterization of $[Cr(gly)_2OH]_2$,

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where gly is glycinato (Hodgson *et al.*, 1972; Veal, Hatfield, Jeter, Hempel & Hodgson, 1973). In this complex the value of φ is 98·2 (2)° and $2J=-8{\cdot}4$ cm^{-1} (Earnshaw & Lewis, 1961; Hodgson *et al.*, 1972). In order to test the generality of our hypothesis concerning the correlation of J and φ, which is based on the principles of super-exchange (Goodenough, 1963), it was necessary to investigate the structure of another chromium dimer of this general type; from the bridged geometry we should be able to make qualitative predictions concerning the sign and magnitude of $2J$. Hence we have undertaken a complete three-dimensional structural investigation of the complex in which L = 1, 10-phenanthroline, *i.e.* the complex $[\mathrm{Cr(phen)_2OH}]_2^{4+}$, as the chloride salt. The choice of this complex results in part from our ability to grow a high quality single crystal of sufficient size to permit us (or others) to undertake single-crystal e.p.r. studies as well as magnetic susceptibility measurements.

Experimental

Suitable red single crystals of the chloride salt were obtained by preparation of the nitrate salt by minor modification of the method of Inskeep & Benson (1961), and recrystallization from aqueous (pH = 6·5) medium which was 0·5 M in potassium chloride. The crystals slowly lose water on exposure to the atmosphere, especially in warm weather, but can be kept indefinitely under the mother liquor.

The crystals were assigned to the triclinic system after examination by precession and Weissenberg photography. No systematic absences were observed, and the space group was identified as either $P\bar{1}$ or $P1$. Examination of a Wilson plot suggested to us that the centrosymmetric space group is correct. The cell constants, obtained by the least-squares method of Busing & Levy (1967), are $a=14{\cdot}056$ (7), $b=11{\cdot}296$ (6), $c=18{\cdot}990$ (9) Å, $\alpha=87{\cdot}15$ (3), $\beta=107{\cdot}63$ (2), and $\gamma=74{\cdot}68$ (3)°; these observations were made at 20 °C with the wavelength assumed as $\lambda(\mathrm{Mo}\ K\alpha_1)=0{\cdot}7093$ Å. The density of 1·342 g cm^{-3} calculated for two dimeric formula units is in reasonable agreement with a measured value 1·39 (4) g cm^{-3} obtained by flotation in carbon tetrachloride/dichloromethane solutions. (The measurement of the density was hindered by our inability to find a solvent mixture of the appropriate density which was completely inert.) Hence, with two formula units in the cell, no crystallographic symmetry is imposed on the dimers.

Intensity data were collected from a hexagonal prismatic crystal of dimensions $0{\cdot}060\times0{\cdot}014\times0{\cdot}023\times0{\cdot}021$ cm. The crystal was mounted along the long axis of the prism, which is roughly perpendicular to the (110) planes. The crystal mosaicity was examined in the usual way (Furnas, 1957) and was found to be acceptable. Data were collected in the manner described previously (Meyer *et al.*, 1972), the θ–2θ scans being from $-0{\cdot}7°$ from the $K\alpha_1$ peak to $+0{\cdot}7°$ from the $K\alpha_2$ peak position. The diffracted beam was filtered through a 1·5 mm Nb foil, which is sufficient to reduce the intensity of the $K\beta$ radiation to approximately zero while reducing the $K\alpha$ intensity by 42 % (Veal & Hodgson, 1972*a*). A unique data set of 5016 independent intensities having $2\theta(\mathrm{Mo})\le40°$ was obtained.

The data were processed in the manner described elsewhere (Corfield, Doedens & Ibers, 1967; Veal & Hodgson, 1972*b*). The value of p in the expression (Busing & Levy, 1957)

$$\sigma(I)=[C+0{\cdot}25(\mathrm{ts/tb})^2(B_H+B_L)+(pI)^2]^{1/2}$$

was assigned as 0·04. No absorption correction was applied. The linear absorption coefficient for this compound with Mo $K\alpha$ radiation is 11·0 cm^{-1}, and trial calculations on the specimen used indicated that neglect of absorption effects would not introduce any error in intensity of greater than ± 3 %.

Solution and refinement

The structure was solved by the heavy atom (Patterson) technique, and refined by least-squares procedures. All least-squares calculations were carried out on F, using J. A. Ibers's *NUCLS* program, with the function minimized being $\sum w(|F_o|-|F_c|)^2$ and the weights w assigned as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c the atomic scattering factors for Cr and Cl were taken from Cromer & Waber (1965), those for C, N, and O from Ibers (1962), and for H from Stewart, Davidson & Simpson (1965). The effects of anomalous dispersion on F_c (Ibers & Hamilton, 1964) were included, the values of $\Delta f'$ and $\Delta f''$ for Cr and Cl being taken from Cromer (1965).

The two independent chromium atoms were located from a three-dimensional Patterson function; three cycles of least-squares refinement, using the scale factor derived from the Wilson plot, gave agreement values $R_1=\sum|F_o|-|F_c|/\sum|F_o|$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$ of 0·547 and 0·611 respectively. In the initial stages of the refinement only the 3176 independent data whose intensities were greater than three times their estimated standard deviations and for which $2\theta(\mathrm{Mo})$ was less than 37·5° were used. The bridging oxygen atoms, the chlorine anions, and the carbon and nitrogen atoms of the phenanthroline ligands were located in subsequent difference Fourier syntheses; the Fourier program used was a modification of Zalkin's *FORDAP*. Least-squares refinement of these atoms, with variable anisotropic thermal parameters assigned to Cr, Cl and O and isotropic parameters to C and N gave values of 0·191 and 0·230 for R_1 and R_2, respectively. Several peaks were found in a subsequent difference Fourier summation which might be assigned as water molecules and the three largest peaks were included in a least-squares refinement. In an attempt to reduce the number of variables in the least-squares calculation we refined the phenanthroline ligands as groups, restricting them to the average geometry found by Frenz & Ibers (1972) for these ligands in $Ni(phen)_3^{2+}$. This calculation caused R_1 and R_2 to increase to 0·294 and 0·379, and led to extremely high thermal parameters for some of the group atoms. We concluded that the geometries of the phenanthroline rings in this structure are not amenable to group refinement because of small, but significant, differences between nominally equivalent bond lengths in the four independent ligands; this was also the case in $Ni(phen)_3[Mn(CO)_5]_2$ (Frenz & Ibers 1972). In all subsequent calculations the ligand atoms were treated individually.

It was also apparent from this calculation that the thermal parameters of the three water molecules were higher than anticipated, which suggested that there may be disorder among the water molecules. A least-squares calculation was run in which the eight highest peaks in the difference Fourier map were included as half-occupancy water oxygen atoms; this calculation yielded $R_1=0·120$ and $R_2=0·173$. Examination of a subsequent difference Fourier map suggested that the two remaining water oxygen atoms were disordered over eight positions. A least-squares calculation based on these positions gave $R_1=0·084$ and $R_2=0·105$; the hydrogen atoms of the phenanthroline ligands and the bridges were included in this calculation, their positions being calculated by assuming C–H bond distances of 1·0 Å and O–H distances of 0·85 Å, and were verified in the difference Fourier map. The thermal parameters of the H atoms were fixed at 4·5 $Å^2$.

An examination of the data at this stage showed that the low angle data all had $|F_o|$ greater than $|F_c|$; this effect, which has been observed in other data sets (Manojlovic-Muir, Muir & Ibers, 1970; Hodgson, Hale & Hatfield, 1971), is the result of an inability to estimate correctly the low-angle background for low-order reflections when Nb filters are used (Veal & Hodgson, 1972*a*). All reflections having 2θ less than 12·5° were removed from the refinement, but the data with 2θ greater than 37·5° were included at this stage; this gave a total of 3392 intensities greater than three times their e.s.d.'s. Least-squares refinement using these data gave $R_1=0·077$ and $R_2=0·087$ for the 297 variables. Any attempt to refine the ligand atoms anisotropically would have introduced a further 280 variables, and this was considered to be unjustified.

Table 1. *Positional and thermal parameters for the non-ring atoms in* $[(phen)_2Cr(OH)]_2Cl_4.6H_2O$

All values (except *B*) are × 10^4.

	Occupancy*	*x*	*y*	*z*	β_{11}†	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	2	−829 (1)	2188 (1)	2362 (1)	52 (1)	63 (1)	21 (1)	−26 (1)	8 (1)	−1 (1)
Cr(2)	2	377 (1)	493 (1)	−2133 (1)	52 (1)	64 (1)	21 (1)	−26 (1)	8 (1)	−1 (1)
O(1)	2	−49 (5)	1006 (5)	1894 (3)	49 (5)	62 (7)	21 (2)	−21 (5)	17 (3)	−6 (3)
O(2)	2	−1183 (5)	698 (5)	2569 (3)	54 (5)	61 (7)	25 (3)	−20 (5)	19 (3)	−7 (3)
Cl(1)	2	4684 (2)	4475 (3)	−1745 (2)	80 (3)	149 (4)	44 (1)	−31 (3)	13 (2)	4 (2)
Cl(2)	2	−2109 (3)	180 (4)	3700 (2)	147 (4)	222 (6)	53 (2)	−60 (4)	52 (2)	1 (2)
Cl(3)	2	1541 (3)	5045 (3)	3698 (2)	113 (3)	145 (4)	50 (2)	−40 (3)	24 (2)	−18 (2)
Cl(4)	2	580 (3)	1927 (3)	646 (2)	111 (3)	169 (4)	31 (1)	−69 (3)	25 (1)	−11 (2)

Table 1 (*cont.*)

	Occupancy	*x*	*y*	*z*	*B* ($Å^2$)
O(3)	1	2652 (9)	1985 (10)	1777 (7)	3·4 (3)
O(4)	1	−4791 (16)	1690 (18)	−1984 (12)	6·3 (6)
O(5)	1	3731 (10)	4047 (12)	4908 (7)	4·5 (3)
O(6)	1	4460 (10)	1909 (11)	1465 (7)	4·2 (3)
O(7)	1	−3397 (12)	345 (14)	−2612 (8)	6·3 (4)
O(8)	1	3866 (11)	105 (13)	−2147 (8)	5·0 (3)
O(9)	1	4762 (11)	3529 (13)	2511 (8)	5·0 (3)
O(10)	1	2790 (10)	3815 (11)	2653 (7)	4·2 (3)
O(11)	0·5	−4173 (17)	1905 (20)	3771 (12)	2·9 (5)
O(12)	0·5	3735 (21)	2572 (24)	−3825 (15)	4·6 (6)
O(13)	0·7	−4622 (24)	4252 (33)	4413 (18)	6·6 (10)
O(14)	0·5	−4884 (42)	515 (57)	−3890 (31)	10·5 (17)
O(15)	0·5	−4997 (45)	11 (61)	3976 (33)	11·7 (19)
O(16)	0·3	5269 (62)	3782 (82)	4265 (45)	8·4 (26)
O(17)	0·5	−5083 (34)	1546 (41)	−5058 (25)	10·3 (11)
O(18)	0·5	4781 (17)	1980 (18)	−2366 (13)	4·1 (4)

* The occupancies of the atomic positions are expressed in atoms per unit cell.

† The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

A difference Fourier synthesis gave no indication of the locations of the hydrogen atoms in the disordered water molecules, there being no peak higher than 0·4 e $Å^{-3}$ in the map. In the last least-squares cycle, the highest shift of any atomic positional parameter was approximately 0·2 times its estimated standard deviation, and this was taken as evidence that the refinement had converged. The value of R_2 showed no dependence in $\sin\theta$ or on $|F_o|$, which indicates that our assignment of $p=0·04$ in the weighting scheme (*vide supra*) is essentially correct. Examination of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is appropriate.

The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables 1 and 2. The final values of $|F_o|$ and $|F_c|$ (in electrons) are shown in Table 3; only the 3392 data that were used in the final refinement are listed in the Table.

Description of the structure

The structure consists of dimeric $[Cr(phen)_2OH]_2^{4+}$ cations which are well separated from chloride anions and water molecules. The geometry of the cation is shown in Fig. 1, and the inner coordination sphere around the chromium atoms is depicted in Fig. 2. The geometry around each chromium atom is roughly octahedral, with two *cis*-phenanthroline ligands and two *cis*-hydroxo groups. The internuclear distances and angles in the cation are given in Table 4.

The eight independent Cr–N separations are in the range 2·031 (8) to 2·072 (8) Å, with an average value of 2·052 (6) Å; the average Cr(1)–N separation is equal to the average Cr(2)–N distance, which suggests that the coordination geometries about the chromium atoms are very similar. This average distance of 2·052 (6) Å is comparable to the values of 2·061 (5) and 2·066 (5) Å in $[Cr(gly)_2OH]_2$ (Veal, Hatfield, Jeter, Hempel & Hodgson, 1973), 2·075 (2) and 2·081 (5) Å in $Cr(en)_3^{3+}$ (Raymond, Corfield & Ibers, 1968; Raymond & Ibers, 1968), the mean value of 2·068 (1) Å in $Cr(gly)_3 . H_2O$ (Bryan, Greene, Stokely & Wilson, 1971) and the

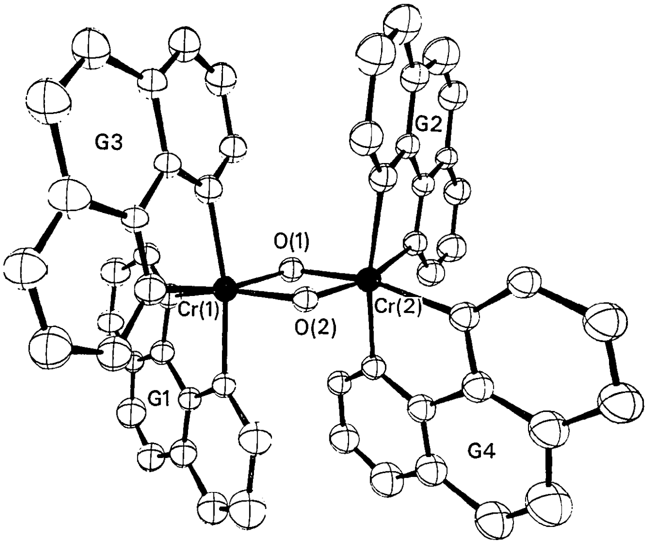


Fig. 1. View of the $[Cr(phen)_2OH]_2^{4+}$ cation. O(1) and O(2) are the oxygen atoms of the bridging hydroxyl groups; G1 *etc.* correspond to phen 1 *etc.* in the text. Hydrogen atoms are omitted for clarity.

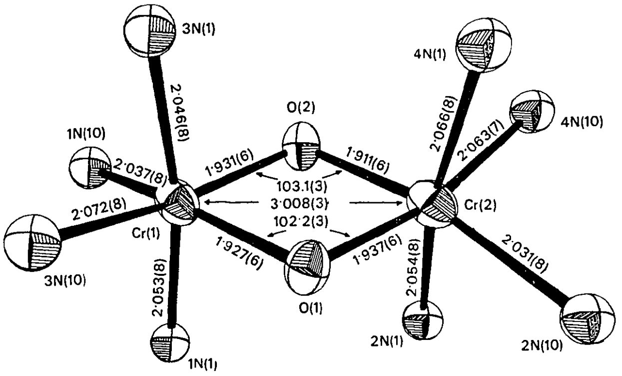


Fig. 2. The coordination around the chromium(III) atoms in $[Cr(phen)_2OH]_2^{4+}$. Atom 3N(1) is nitrogen 1 of group phen 3, *etc.*

Table 2. *Positional* ($\times 10^4$) *and thermal parameters for the* 1,10-*phenanthroline groups*

	x	*y*	*z*	*B*(Å^2)
Phen 1				
N(1)	518 (6)	1919 (7)	3246 (4)	3·23 (16)
C(2)	1512 (8)	1371 (9)	3281 (6)	3·61 (22)
C(3)	2355 (9)	1230 (10)	3937 (7)	4·89 (26)
C(4)	2176 (9)	1686 (10)	4558 (6)	4·69 (26)
C(5)	895 (9)	2874 (11)	5130 (7)	5·11 (27)
C(6)	−80 (10)	3462 (11)	5068 (7)	4·91 (26)
C(7)	−1962 (9)	4197 (10)	4292 (6)	4·68 (25)
C(8)	−2705 (9)	4234 (10)	3619 (7)	4·90 (26)
C(9)	−2405 (8)	3663 (10)	3035 (6)	4·13 (24)
N(10)	−1424 (6)	3102 (7)	3104 (4)	3·42 (17)
C(11)	−692 (8)	3048 (9)	3789 (6)	3·43 (22)
C(12)	360 (7)	2405 (9)	3860 (5)	3·07 (21)
C(13)	1168 (8)	2301 (9)	4534 (6)	3·70 (23)
C(14)	−917 (8)	3579 (9)	4392 (6)	3·69 (23)
Phen 2				
N(1)	−765 (6)	1109 (7)	−3156 (4)	3·30 (16)
C(2)	−708 (8)	863 (9)	−3832 (6)	3·78 (23)
C(3)	−1573 (9)	1307 (10)	−4479 (6)	4·24 (24)
C(4)	−2474 (9)	2016 (11)	−4438 (7)	4·97 (26)
C(5)	−3479 (9)	3102 (11)	−3649 (7)	4·95 (26)
C(6)	−3481 (9)	339 (11)	−2973 (7)	5·34 (28)
C(7)	−2527 (8)	3283 (10)	−1626 (6)	4·15 (24)
C(8)	−1616 (8)	2792 (9)	−1051 (6)	3·61 (22)
C(9)	−759 (8)	1980 (9)	−1166 (6)	3·38 (21)
N(10)	−765 (6)	1662 (7)	−1839 (4)	3·16 (16)
C(11)	−1699 (8)	2175 (9)	−2413 (6)	3·22 (21)
C(12)	−1665 (7)	1845 (8)	−3114 (5)	2·84 (20)
C(13)	−2565 (8)	2310 (10)	−3748 (6)	4·21 (24)
C(14)	−2586 (8)	2955 (9)	−2324 (6)	3·59 (22)
Phen 3				
N(1)	−2210 (6)	2793 (7)	1498 (4)	3·32 (17)
C(2)	−3032 (8)	2349 (9)	1366 (6)	3·89 (23)
C(3)	−3911 (9)	2822 (10)	704 (6)	4·46 (25)
C(4)	−3909 (8)	3677 (10)	192 (6)	4·26 (24)
C(5)	−3001 (9)	5143 (10)	−179 (6)	4·32 (24)
C(6)	−2212 (9)	5570 (10)	−15 (6)	4·29 (24)
C(7)	−486 (9)	5573 (11)	893 (7)	4·93 (26)
C(8)	274 (9)	5105 (11)	1565 (7)	5·15 (27)
C(9)	208 (8)	4153 (9)	2036 (6)	4·09 (24)
N(10)	−629 (6)	3705 (7)	1830 (4)	3·28 (17)
C(11)	−1387 (7)	4186 (9)	1168 (5)	2·92 (20)
C(12)	−2245 (7)	3706 (9)	979 (5)	2·95 (20)
C(13)	−3080 (8)	4173 (9)	313 (6)	3·26 (21)
C(14)	−1353 (8)	5126 (9)	671 (6)	3·75 (23)
Phen 4				
N(1)	1488 (6)	214 (7)	−1090 (4)	3·11 (16)
C(2)	1656 (8)	−555 (9)	−477 (6)	3·55 (22)
C(3)	2482 (8)	−687 (9)	178 (6)	3·88 (23)
C(4)	3158 (8)	−4 (10)	216 (6)	4·00 (23)
C(5)	3669 (9)	1587 (10)	−424 (6)	4·16 (25)
C(6)	3460 (9)	2394 (10)	−1026 (6)	4·55 (25)
C(7)	2285 (8)	3434 (9)	−2300 (6)	3·92 (23)
C(8)	1422 (9)	3536 (10)	−2871 (6)	4·35 (25)
C(9)	799 (8)	2730 (9)	−2856 (6)	3·81 (23)
N(10)	1072 (6)	1847 (7)	−2264 (4)	3·17 (16)
C(11)	1931 (7)	1776 (9)	−1684 (5)	2·88 (20)
C(12)	2162 (7)	911 (8)	−1035 (5)	2·88 (20)
C(13)	3016 (8)	810 (9)	−412 (6)	3·39 (22)
C(14)	2573 (8)	2554 (9)	−1670 (6)	3·46 (22)

Table 3. *Observed and calculated structure amplitudes* (*in electrons*) *for* $[Cr(phen)_2OH]_2Cl_4.6H_2O$

h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc	h	k	l	fo	fc

Table 3 (*cont.*)

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc

average value of 2·08 (1) Å for the *cis* Cr–N lengths in $[Cr(NH_3)_5(OH)Cr(NH_3)_5]^{5+}$ (Veal, Jeter, Hempel, Eckberg, Hatfield & Hodgson, 1972); the absence of any appreciable shortening of the Cr–N distance in $[Cr(phen)_2OH]_2^{4+}$ relative to these other separations suggests that there is very little multiple bonding here between Cr and the aromatic ligand. The Cr–N distances also correlate well with the Ni(II)–N and Co(III)–N lengths in $Ni(phen)_3^{2+}$ (Frenz & Ibers, 1972) and $[Co(S_2C_2(CN)_2)_2\text{-}(phen)]^-$ (Khare & Eisenberg, 1970). The average Ni–N distance in $Ni(phen)_3^{2+}$ is 2·090 (5) Å, or 0·038 Å longer than the average Cr–N value here, while the average Co–N distance is 2·009 (12) Å, or 0·043 Å shorter than our Cr–N distance; this observed order of the M–N distances is that predicted from the covalent radii of the metal atoms (Pauling, 1960).

The Cr–O distances in the bridge are in the range 1·911 (6) to 1·937 (6) Å, with an average value of 1·927 (6) Å. These values are significantly shorter than the values of 1·966 (4) and 1·968 (4) Å in $[Cr(gly)_2OH]_2$ (Veal, Hatfield, Jeter, Hempel & Hodgson, 1973), but are similar to the average values of 1·916 and 1·922 Å for the Cu–O bridging distances in $[Cu(EAEP)OH]_2^{2+}$ (Lewis *et al.*, 1972) and $[Cu(bipy)OH]_2^{2+}$ (Majeste & Meyers, 1970). The Cr–O–Cr–O bridging unit is roughly planar, with all atoms lying within 0·015 Å of the least-squares plane through the four atoms; the least-squares planes were calculated using Doedens' program *PLANET*. The Cr–Cr separation is 3·008 (3) Å, which is slightly longer than the value of 2·974 (2) Å in $[Cr(gly)_2OH]_2$ and is very similar to the value of 3·000 (4) Å for the Cu–Cu separation in $[Cu(tmen)_2OH]_2^{2+}$ (Mitchell *et al.*, 1970). This increase in the Cr–Cr distance relative to the glycinato complex is brought about by an increase in the Cr–O–Cr bridging angles; the values of 102·2 (3) and 103·1 (3)° here are considerably larger than the angle of 98·2 (2)° found in $[Cr(gly)_2OH]_2$. In view of the observed inverse correlation between the bridging angle, φ, and the singlet-triplet splitting, $2J$, in the copper(II) dimers $[CuL_2(OH)]_2^{n+}$ (Lewis *et al.*, 1972), we would predict that $[Cr(phen)_2OH]_2^{4+}$ would have a singlet ground state with a value of $2J$ considerably smaller than the $-8·4\ cm^{-1}$ found in $[Cr(gly)_2OH]_2$, *i.e.*, since J is negative, the magnitude of $2J$ should be much larger than $8·4\ cm^{-1}$. Earnshaw & Lewis (1961) have reported the magnetic susceptibility of the iodide salt of $[Cr(phen)_2OH]_2^{4+}$ in the range 93·5 to 292°K, and conclude that the ground state is a singlet with $2J = -13\ cm^{-1}$; while this value is in the anticipated direction, we would expect that the chloride salt would show a magnitude of $2J$ which is considerably greater than this reported value for the iodide, and preliminary data in the range 4·2 to 295°K support our conclusion (Hempel, Jeter, Veal, Hodgson & Hatfield, 1972). We conclude that either the value of φ in the iodide salt is smaller than in the chloride, or that low temperature susceptibility measurements on the iodide will produce a significantly different value of $2J$: it should be noted that the susceptibility maximum of these complexes occurs considerably below 90°K, and that Earnshaw & Lewis were forced to deduce the value of $2J$ from fitting procedures.

The distances and angles found in the four independent 1,10-phenanthroline ligands are listed in Tables 5 and 6. Also shown in Table 5 are the fractions of π bond character calculated from valence-bond theory by Pauling (1960) for the parent hydrocarbon molecule, phenanthrene. As was also observed in the

Table 4. *Selected intramolecular distances and angles for the* Cr(III) *coordination sphere*

Intramolecular distances (Å)

Cr(1)–Cr(2)	3·008 (3)	Cr(1)–3N(1)	2·046 (8)
Cr(1)–O(1)	1·927 (6)	Cr(1)–3N(10)	2·072 (8)
Cr(1)–O(2)	1·911 (6)	Cr(2)–2N(1)	2·045 (8)
Cr(2)–O(1)	1·937 (6)	Cr(2)–2N(10)	2·031 (8)
Cr(2)–O(2)	1·931 (6)	Cr(2)–4N(1)	2·066 (8)
Cr(1)–1N(1)	2·053 (8)	Cr(2)–4N(10)	2·063 (7)
Cr(1)–1N(10)	2·037 (8)		

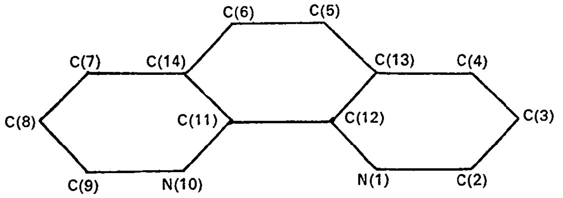
Intramolecular angles (°)

O(1)—Cr(1)–O(2)	77·2 (2)	Cr(1)—O(1) –Cr(2)	102·2 (3)
O(1)—Cr(2)–O(2)	77·4 (2)	Cr(1)—O(2) –Cr(2)	103·1 (3)
1N(1)—Cr(1)–1N(10)	79·9 (3)	2N(1)—Cr(2)–2N(10)	79·3 (3)
1N(1)—Cr(1)–O(1)	88·7 (3)	2N(1)—Cr(2)–O(1)	98·1 (3)
1N(1)—Cr(1)–O(2)	101·3 (3)	2N(1)—Cr(2)–O(2)	90·0 (3)
1N(1)—Cr(1)–3N(1)	169·5 (3)	2N(1)—Cr(2)–4N(1)	169·5 (3)
1N(1)—Cr(1)–3N(10)	93·4 (3)	2N(1)—Cr(2)–4N(10)	92·6 (3)
1N(10)–Cr(1)–O(1)	164·7 (3)	2N(10)–Cr(2)–O(1)	95·9 (3)
1N(10)–Cr(1)–O(2)	94·7 (3)	2N(10)–Cr(2)–O(2)	166·6 (3)
1N(10)–Cr(1)–3N(1)	94·0 (3)	2N(10)–Cr(2)–4N(1)	94·4 (3)
1N(10)–Cr(1)–3N(10)	96·8 (3)	2N(10)–Cr(2)–4N(10)	93·5 (3)
3N(1)—Cr(1)–3N(10)	78·8 (3)	4N(1)—Cr(2)–4N(10)	79·3 (3)
3N(1)—Cr(1)–O(1)	98·7 (3)	4N(1)—Cr(2)–O(1)	90·8 (3)
3N(1)—Cr(1)–O(2)	88·9 (3)	4N(1)—Cr(2)–O(2)	97·3 (3)
3N(10)–Cr(1)–O(1)	94·0 (3)	4N(10)–Cr(2)–O(1)	166·9 (3)
3N(10)–Cr(1)–O(2)	163·7 (3)	4N(10)–Cr(2)–O(2)	95·1 (3)

cases of Ni(phen)$_3^{2+}$ (Frenz & Ibers, 1972) and [Co(S$_2$C$_2$(CN)$_2$)phen]$^-$ (Khare, Pierpont & Eisenberg, 1968; Khare & Eisenberg, 1970), the average values of the C–C and C–N bonds in the phenanthroline rings correlate quite well with Pauling's π bond orders; thus, for example, the longest C–C bonds are C(5)–C(13), C(6)–C(14) and C(11)–C(12), which have only $\frac{1}{5}$ double-bond character, while the shortest C–C bond is C(5)–C(6), which has $\frac{4}{5}$ double-bond character.

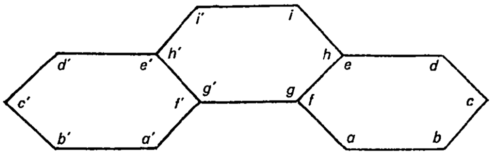
Frenz & Ibers (1972) have noted that there is a correlation between the metal–nitrogen bond distance and the angle subtended by the nitrogen atoms at the metal since the N···N separation in phenanthroline is inflexible. In two recently reported Co(III) complexes the bites of the phenanthroline ligands were 2·72 (2) Å and 2·63 (3) Å (Khare & Eisenberg, 1970; Pierpont & Eisenberg, 1970), in Ni(phen)$_3^{2+}$ it is 2·66 (1) Å and in the present case it is 2·621 (7) Å; these four values do not appear to differ significantly, which is consistent with this concept.

Table 5. *Bond distances* (Å) *in the* 1,10-*phenanthroline ligands of* [(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]$^{4+}$



	Phen 1	Phen 2	Phen 3	Phen 4	Average	π order
N(1)—N(10)	2·626 (9)	2·607 (9)	2·613 (9)	2·636 (9)	2·621 (6)	—
N(1)—C(2)	1·350 (12)	1·349 (12)	1·339 (12)	1·338 (11)	1·344 (8)	0·6
C(2)—C(3)	1·404 (14)	1·397 (14)	1·427 (14)	1·390 (13)	1·405 (9)	0·4
C(3)—C(4)	1·375 (15)	1·335 (14)	1·338 (14)	1·361 (13)	1·352 (9)	0·6
C(4)—C(13)	1·389 (14)	1·403 (15)	1·386 (13)	1·401 (13)	1·395 (9)	0·4
C(13)–C(5)	1·432 (15)	1·428 (15)	1·453 (14)	1·431 (14)	1·436 (10)	0·2
C(5)—C(6)	1·321 (15)	1·340 (15)	1·284 (13)	1·333 (14)	1·320 (10)	0·8
C(6)—C(14)	1·427 (15)	1·420 (15)	1·438 (14)	1·420 (14)	1·426 (10)	0·2
C(14)–C(7)	1·399 (14)	1·380 (14)	1·397 (14)	1·401 (13)	1·394 (9)	0·4
C(7)—C(8)	1·374 (14)	1·362 (13)	1·363 (15)	1·332 (13)	1·358 (9)	0·6
C(8)—C(9)	1·427 (15)	1·391 (13)	1·405 (15)	1·425 (14)	1·412 (10)	0·4
C(9)—N(10)	1·320 (12)	1·343 (12)	1·359 (12)	1·354 (11)	1·344 (8)	0·6
N(10)–C(11)	1·379 (12)	1·383 (11)	1·352 (11)	1·345 (12)	1·365 (7)	0·4
C(11)–C(12)	1·426 (13)	1·412 (13)	1·407 (13)	1·432 (13)	1·419 (9)	0·2
C(12)–N(1)	1·365 (11)	1·345 (11)	1·371 (11)	1·367 (11)	1·362 (7)	0·4
C(12)–C(13)	1·406 (13)	1·410 (13)	1·401 (13)	1·380 (13)	1·399 (9)	0·4
C(11)–C(14)	1·400 (13)	1·386 (13)	1·405 (13)	1·412 (13)	1·401 (9)	0·4

Table 6. *Bond angles in the* 1,10-*phenanthroline ligands of* [(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]$^{4+}$



Bond angle	Phen 1	Phen 2	Phen 3	Phen 4	Average
a	117·7 (8)°	118·7 (8)°	117·9 (8)°	116·2 (8)°	117·3 (5)°
a′	116·4 (8)	115·2 (8)	119·0 (8)	118·1 (8)	117·2 (5)
b	121·6 (9)	121·4 (9)	120·4 (9)	123·1 (9)	121·6 (6)
b′	122·7 (10)	122·9 (9)	120·0 (10)	120·7 (9)	121·6 (6)
c	119·7 (11)	120·0 (10)	120·6 (10)	119·8 (10)	120·0 (7)
c′	120·1 (10)	120·8 (10)	120·6 (11)	120·5 (10)	120·5 (7)
d	120·3 (11)	120·5 (11)	120·7 (10)	119·2 (10)	120·1 (7)
d′	118·7 (10)	118·7 (10)	120·2 (11)	120·2 (10)	119·5 (7)
e	117·0 (10)	117·0 (10)	116·7 (9)	117·5 (9)	117·1 (6)
e′	117·4 (10)	118·1 (10)	116·8 (9)	117·0 (9)	117·3 (6)
f	123·5 (9)	122·2 (9)	123·6 (8)	124·1 (8)	123·4 (6)
f′	124·7 (9)	124·3 (9)	123·3 (9)	123·5 (8)	124·0 (6)
g	120·1 (9)	119·2 (9)	121·0 (9)	120·7 (9)	120·3 (6)
g′	119·8 (9)	122·3 (9)	119·5 (9)	118·9 (9)	120·1 (6)
h	117·8 (9)	118·1 (10)	117·0 (9)	118·9 (9)	118·0 (7)
h′	118·8 (10)	116·8 (10)	118·2 (9)	118·5 (9)	118·1 (7)
i	122·3 (11)	121·0 (11)	122·2 (10)	120·7 (10)	121·6 (7)
i′	121·2 (11)	122·6 (11)	122·1 (10)	122·1 (10)	122·0 (7)

The deviations of the atoms from the least-squares planes through the phenanthroline ligands are tabulated in Table 7. There are clearly significant deviations from planarity in some of the rings, especially in phen 4, but we are unable to discern any significant trend. This non-planarity of phenanthroline groups has also been observed by several other workers (Graham & Fenn, 1970; Preston & Kennard, 1969*a*, *b*; Pierpont & Eisenberg, 1970; Khare & Eisenberg, 1970; Frenz & Ibers, 1972). The chromium atoms do not lie in these least-squares planes; thus Cr(1) is 0·07 and 0·28 Å out of the planes through phen 1 and phen 3, respectively, while Cr(2) is 0·28 and 0·18 Å from those through phen 2 and phen 4, respectively.

Table 7. *Distances* (Å) *of the atoms from their respective planes for the* 1,10-*phenanthroline*

Atom	Phen 1	Phen 2	Phen 3	Phen 4
N(1)	−0·027	−0·044	0·051	0·072
C(2)	0·036	0·058	−0·002	−0·026
C(3)	0·029	0·074	−0·078	−0·095
C(4)	−0·017	0·028	−0·015	−0·062
C(5)	−0·004	−0·029	0·004	0·021
C(6)	0·010	−0·013	0·005	0·034
C(7)	0·022	0·077	−0·012	−0·047
C(8)	0·008	0·075	−0·043	−0·083
C(9)	−0·017	−0·012	−0·027	−0·039
N(10)	0·005	−0·052	0·016	0·053
C(11)	−0·008	−0·049	0·027	0·064
C(12)	−0·019	−0·056	0·038	0·062
C(13)	−0·027	−0·044	0·020	0·037
C(14)	0·009	−0·012	0·017	0·010

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