

Preparation and Crystal Structure of $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$): The First Chromous Halide-Disilicates

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The new chromous oxo-halides $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) which adopt a hitherto unknown structure type were obtained as small, deep blue crystals from mixtures of Cr_2O_3 , Cr , SiO_2 , and CrCl_3 or CrBr_2 , respectively, in sealed silica tubes at elevated temperatures ($\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$: 1000°C; $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$: 1220°C) in the presence of a mineralizer (NH_4Cl ; excess of CrBr_2). They show remarkable stability against oxidation. The crystal structures of both $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ ($\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$) have been determined and refined from X-ray single crystal data (*Pc* No. 7), $Z = 4$, $a = 6.3853(7)$ Å (6.414(3) Å), $b = 12.707(2)$ Å (12.829(6) Å), $c = 10.448(1)$ Å (10.540(6) Å), $\beta = 92.37(1)^\circ$ (91.61(4)°). Four circle diffractometer data were used for the refinement of the chloride structure while imaging plate data were used for the bromide (conventional residual $R1 = 0.016$ (0.053) for 4761 (3491) $F_o > 4\sigma$, 4945 (3911) independent reflections, 273 (273) parameters). The structure consists of eight crystallographically different Cr^{2+} with c.n. five or six and mixed coordination by oxygen and halogen. All coordination polyhedra are highly distorted as a result of the Jahn–Teller effect. Two independent disilicate groups exhibit almost eclipsed conformation with bridging angles (Si–O–Si) of 145.8° and 138.4° for the chloride and 146.3° and 140.8° for the bromide. © 1996 Academic Press

INTRODUCTION

Until now there has been little information available on chromium(II) containing oxo-compounds, like phosphates, borates, silicates, or “salts” of other oxo-acids. The tendency of Cr^{2+} to disproportionate into Cr^0 and Cr^{3+} is probably the reason for the small number of chromium(II)-oxo-compounds known so far. Among the few well-characterized compounds of divalent chromium coordinated only by oxygen or oxygen and halogen atoms are the boracites $\text{Cr}_3\text{B}_7\text{O}_{13}\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (1–3), $\text{CaCrSi}_4\text{O}_{10}$ (4), the mixed-valent chromium(II, III)-phosphates $\text{Cr}_6(\text{P}_2\text{O}_7)_4$ (5) and $\text{Cr}_7(\text{PO}_4)_6$ (6), and Cr_2SiO_4 , the structure of which has been determined only recently (7). On the other hand, there is an interest in such compounds for the particular stereochemistry related to the d^4 electronic configuration of divalent chromium and the resulting

Jahn–Teller effect. For investigations on magnetic properties, crystal chemistry, and correlation between color and coordination geometry around Cr^{2+} we tried to synthesize new compounds containing $\text{Cr}(\text{II})$.

First information on chromous halide-silicates dates back to the thirties, when Doerner observed a blue, silicate-containing compound after reaction of CrCl_2 with quartz glass at temperatures above 900°C (8), but did not report any further characterization. Fischer (9) found at the same time that at its melting temperature (842°C) CrBr_2 does not react with quartz. In this paper we report on preparation and crystal structure of the first chromous halide-disilicates. Possibly, the deep-blue chloride-disilicate we describe here is the same Doerner had already observed.

EXPERIMENTAL

Single crystals of the chromous dichloride-disilicate were obtained following Eq. [1] by reacting stoichiometric mixtures of Cr_2O_3 (Merck), Cr (Johnson Matthey Chemicals), SiO_2 (Serva), and CrCl_3 (Fluka) in evacuated silica-ampoules with a small amount of NH_4Cl added as mineralizer.



The ampoules were heated in a temperature gradient $T_2 \approx 1000^\circ\text{C}$ and $T_1 \approx 900^\circ\text{C}$, with the starting materials at the higher temperature. After ca. 5 days, deep blue transparent crystals had formed in the middle of the ampoules. No reversible chemical transport behaviour was observed. The crystals were attached to the walls of the ampoules and had to be scratched off mechanically since they slowly dissolve in 5% HF. There was also Cr_2O_3 attached to the crystals and especially at higher temperatures ($T_2 > 1000^\circ\text{C}$) the chloride-disilicate was partly molten and sometimes it had grown into the walls of the ampoule.

For the preparation of chromous dibromide-disilicate the calculated amounts of SiO_2 , Cr_2O_3 , Cr and about 20% excess of CrBr_2 were filled into thick-walled (3 mm) silica

ampoules and heated at a higher temperature (1220°C; 30 h) than those necessary for the chloride-disilicate.



Besides a purple compound containing less bromide (presumably $\text{Cr}_2\text{SiO}_4 \cdot 1/8\text{CrBr}_2$ (10)), a small amount of deep-blue crystals of $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$ had formed. No reaction of the starting materials has been found below 1200°C in agreement with the observations of Fischer (9). At temperatures above 1280°C heavy corrosion of the walls of the silica ampoules took place. Both halide-disilicates exhibit remarkable resistance against oxidation. They are stable in air and dilute nitric acid.

STRUCTURE REFINEMENT AND DESCRIPTION

Structure Refinement

Relevant experimental and crystallographic data for $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ and $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$ are listed in Table 1. Systematic absences obtained from precession exposures indicate space groups $P2_1/c$ or Pc . During the structure refinements Pc was confirmed. The noncentrosymmetric structures have been refined using SHELXL-93 (12).¹ The origin has been fixed following the procedure given by Flack and Schwarzenbach (14). Allowance of racemic twinning was given in the refinements according to a method described by Flack and Bernardinelli (15, 16) (volume ratio of enantiomers: 21:79 (chloride); 74:26 (bromide)). Atomic parameters for $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ and $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$ are given in Tables 2 and 3. Projections of the crystal structure (Fig. 1) as well as an inspection of the site parameters (Tables 2 and 3) suggest higher symmetry than Pc for $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ and $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$. We therefore tried, despite the observed extinction conditions, to refine the structures in spacegroup $P2_1/c$ assuming a center of symmetry at (0.69, 0.25, 0.38) of the unit cell chosen in spacegroup Pc . These attempts led to split positions for some atoms (Cr(7) and Cr(8) in Pc) and for all other atoms to highly anisotropic displacement parameters with unreasonable high residuals $R1$ and $wR2$. Structure refinement in spacegroup $P2_1/c$ turned out to be completely impossible.

X-ray Guinier powder-diagrams of the bulk samples are in good agreement with pattern calculated on the basis of structural parameters derived from the single crystal data.

When comparing the data of the chloride-disilicate obtained from an AED-2 four circle diffractometer with those for the bromide-disilicate from IPDS measurements the

better quality of the former is obvious with internal residuals $R(\text{int.}) = 0.021$ and 0.034 for the chloride and the bromide, respectively. The better quality of the data set obtained for $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ is reflected as well in the refinements by a better residual ($R(\text{on F's}) = 1.6\%$ (chloride), 5.3% (bromide)), smaller principle mean square atomic displacement parameters and smaller standard deviations for all parameters.

Crystal Structure

The crystal structure of the chromous halide-disilicates $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{X}_2$ ($X = \text{Cl}, \text{Br}$) consists of halide ions and $[\text{Si}_2\text{O}_7]$ groups forming strongly distorted coordination polyhedra around Cr^{2+} (Fig. 1). Bond lengths and angles are given in Tables 4 and 5. The unit cell contains eight crystallographically different Cr atoms. All show mixed coordination by oxygen and halogen atoms. Figure 1 visualizes that for a better topological understanding the structure might be divided into two types of slightly warped layers parallel to (1 0 0), with one "chromium disilicate" layer and the other layer containing Cr^{2+} and halide. The halide ions form a hexagonal net within such a layer.

The coordination polyhedra around chromium in the "chromium disilicate" layer (Cr1, Cr4, Cr5, and Cr6) have an almost square planar basis of four oxygen atoms. These squares share opposite edges, thus forming chains parallel to the crystallographic b -axis (Fig. 2a). The chains are connected to each other via disilicate groups. It is unusual that Cr5 and Cr6 are even coordinated by the bridging oxygen atoms O11 and O3 in Si_2O_7 -groups. Only relatively long Cr–X bonds connect the "chromous-silicate" with the "chromous-halide" substructure (Fig. 1b and 2b), where Cr2, Cr3, Cr7, Cr8 are mainly coordinated to halogen atoms.

Coordination around Cr^{2+}

While Cr5, Cr6, and Cr8 are coordinated by six ligands, forming strongly distorted octahedra, the other five Cr atoms (Cr1, Cr2, Cr3, Cr5, Cr7) have an environment of only five ligands. Cr6 has five oxygen and only one halogen atom as ligands. Four oxygen atoms with shorter bonds form a slightly bent square plane. Above and below the plane are the remaining ligands X1 and O3 with longer bonds. Cr8 is surrounded by three oxygen and three halogen ions, with one halogen in-plane with the oxygen atoms leading to comparatively long bonds for the remaining halogens above and below the plane. The octahedron around Cr5 formed by five oxygen atoms and one halogen is strongly distorted as a result of the very long bond to O4. In the bromide-disilicate this $d(\text{Cr5-O4})$ is getting even longer (2.926 Å). By further distortion of the octahedra around Cr3, Cr2, and Cr7 one ligand is removed, leaving only five ligands forming crooked trigonal bipyra-

¹ Supplementary material on the structure investigations has been deposited (References: CSD-405842 (chloride), CSD-405843 (bromide)) and can be obtained through FACHINFORMATIONSZENTRUM KARLSRUHE, D-76344 Eggenstein-Leopoldshafen, Germany.

TABLE 1
Summary of Crystallographic Parameters and Details on Measurement, Structure Determination, and Refinement for Cr₄(Si₂O₇)Cl₂ and Cr₄(Si₂O₇)Br₂

Empirical formula	Cr ₄ (Si ₂ O ₇)Cl ₂	Cr ₄ (Si ₂ O ₇)Br ₂
Formula weight	447.1	536.0
Crystal size [mm ³]	ca. 0.15 · 0.15 · 0.15	ca. 0.08 · 0.10 · 0.08
Color	deep blue, transparent	deep blue, transparent
Crystal system	monoclinic	monoclinic
Space group	<i>Pc</i> (No. 7)	<i>Pc</i> (No. 7)
<i>a</i> [Å]	6.3853(7) ^a	6.414(3) ^b
<i>b</i> [Å]	12.707(2)	12.829(6)
<i>c</i> [Å]	10.448(1)	10.540(6)
β [°]	92.37(1)	91.61(4)
Number of formula units <i>Z</i>	4	4
Volume of the unit cell [Å ³]	847.0	866.9
ρ_{calc} [g/cm ³]	3.506	4.107
Diffractometer	four-circle diffractometer AED-2, Fa. Siemens	IPDS imaging plate diffraction system, Fa. Stoe
T [°C]	room temperature	room temperature
λ (MoK α) [Å]	0.71073	0.71073
Absorption correction	empirical correction involving φ -scans	numerical correction, optimized crystal shape with HABITUS (13)
<i>hkl</i> -data limits	$-8 \leq h \leq 8, -17 \leq k \leq 17, -14 \leq l \leq 14$	$-8 \leq h \leq 8, -16 \leq k \leq 16, -13 \leq l \leq 13$
Reflections (range)	9682 ($3.2^\circ \leq 2\theta \leq 60^\circ$)	6375 ($3^\circ \leq 2\theta \leq 56.1^\circ$)
Structure determination	starting positions from Cr ₄ (Si ₂ O ₇)Br ₂ refinement with SHELXL-93 (12)	starting position from Direct Methods by SHELXS-86 (11), refinement with SHELXL-93 (12)
<i>R</i> (int.)	0.021	0.034
Volume ratio of enantiomers	20.9(8):79.1	74(2):26
Number of unique reflections	4945	3911
Number of observed reflections ($I > 4\sigma$ after data merging)	4761	2072
Number of parameters	273	273
Residual electron density $e/\text{\AA}^3$	max.: 0.34 min: -0.44	max.: 2.34 min: -1.24
Goodness of fit	1.068	1.047
$R1 = \frac{\sum(F_o - F_c)}{\sum F_o }$	$R1 = 0.016$	$R1 = 0.053$
$wR2 = \frac{\sum[w(F_o^2 - F_c^2)]}{\sum[w(F_o^2)^{1/2}]}$	$wR2 = 0.042$	$wR2 = 0.144$
Weighting scheme	WGHT: 0.0207 0.1989	WGHT: 0.0736 21.6248
$P = \frac{\max(F_o^2, 0) + 2 \cdot F_c^2}{3}$	$W = \frac{1}{\sigma^2 \cdot F_o^2 + (0.0207 \cdot P)^2 + 0.20 \cdot P}$	$W = \frac{1}{\sigma^2 \cdot F_o^2 + (0.0736 \cdot P)^2 + 21.62 \cdot P}$
Correction for extinction ^c	$f_{\text{Ex}} = 0.0032(2)$	$f_{\text{Ex}} = 0.0051(8)$
Scan mode	ω -scan, learned profile	irradiation time: 26 min per image 183 images; $0 \leq \varphi \leq 182^\circ$

^a From single-crystal measurement on the four-circle diffractometer.

^b From single-crystal measurement on the IPDS.

^c An extinction parameter f_{Ex} is refined, where F_c is multiplied by $k[1 + 0.001 \cdot f_{\text{Ex}} \cdot \lambda^3/\sin(2\theta)]^{-1/4}$ (SHELXL-93 (12)).

mides with the three oxygen atoms in a square plane with one corner missing and the two halogen atoms above and below the plane bending in at the missing corner of the plane. This seems to be the best arrangement for Cr coordinated by two halogen and three oxygen atoms. The remaining Cr1 and Cr4 have only one halogen ligand making the square pyramid with a plane of four oxygens the

favorable arrangement. Figure 3 shows the different coordination polyhedra as ORTEP-plot.

The mean distance of the short Cr–O bonds in the square plane around Cr²⁺ (for Cr₄(Si₂O₇)Cl₂ (Cr₄(Si₂O₇)Br₂)) is 2.057 Å (2.068 Å) (omitting Cr5–O4) while the mean long Cr–O bond is 2.527 Å (2.433 Å) and the mean Cr–X distance is 2.694 Å (2.798 Å). The individual distances can

TABLE 2

Atomic Positions and Isotropic Displacement Parameters of $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$, (Pc , $Z = 4$, $a = 6.3853(7)$ Å, $b = 12.707(2)$ Å, $c = 10.448(1)$ Å, $\beta = 92.37(1)^\circ$)

Atom	x	y	z	U_{eq}
Cr1	0.18372(5)	0.12885(3)	0.39777(3)	0.01056(7)
Cr2	0.81107(5)	0.03351(3)	0.58642(4)	0.01558(7)
Cr3	0.81780(5)	0.72188(3)	0.57379(4)	0.01222(7)
Cr4	0.21783(5)	0.62713(2)	0.88628(3)	0.00966(7)
Cr5	0.20670(6)	0.36369(3)	0.88237(3)	0.01526(7)
Cr6	0.14896(6)	0.88665(3)	0.40482(3)	0.01231(7)
Cr7	0.54722(6)	0.76748(3)	0.07801(4)	0.01240(7)
Cr8	0.56264(5)	0.54127(3)	0.68936(4)	0.01157(7)
Si1	0.06562(9)	0.50389(4)	0.62846(5)	0.0075(1)
Si2	0.05612(8)	0.74037(4)	0.14441(5)	0.0071(1)
Si3	0.32038(9)	0.99882(4)	0.64375(5)	0.0075(1)
Si4	0.32460(8)	0.75984(4)	0.63520(5)	0.0073(1)
O1	0.1208(2)	0.0203(1)	0.5388(1)	0.0095(3)
O2	0.2487(3)	0.0000(1)	0.7889(2)	0.0124(3)
O3	0.3862(3)	0.8805(1)	0.6020(2)	0.0118(3)
O4	0.2539(3)	0.5361(1)	0.7313(2)	0.0144(3)
O5	0.2524(3)	0.7553(1)	0.7798(2)	0.0120(3)
O6	0.5087(2)	0.0765(1)	0.6100(2)	0.0120(3)
O7	0.2234(2)	0.7468(1)	0.0283(1)	0.0091(3)
O8	-0.1371(2)	0.5761(1)	0.6474(2)	0.0117(3)
O9	0.1752(3)	0.7731(1)	0.2771(1)	0.0129(3)
O10	0.1290(2)	0.7360(1)	0.5308(1)	0.0113(3)
O11	0.0078(3)	0.3834(1)	0.6674(2)	0.0145(3)
O12	0.1540(3)	0.5056(1)	0.4855(2)	0.0130(3)
O13	-0.1495(2)	0.8079(1)	0.1083(2)	0.0124(3)
O14	0.5188(2)	0.6843(1)	0.6062(1)	0.0109(3)
Cl1	-0.2506(1)	0.87533(4)	0.43550(5)	0.0142(1)
Cl2	0.6290(1)	0.61432(5)	0.95391(6)	0.0220(1)
Cl3	0.5831(1)	0.37017(4)	0.79242(6)	0.0193(1)
Cl4	-0.1892(1)	0.11917(5)	0.26965(6)	0.0240(1)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j$$

Note. Standard deviations in parentheses.

be derived from Tables 5 and 6. The bromide-disilicate shows very similar coordination polyhedra as the chloride compound, but Cr5 is only coordinated by five ligands because oxygen O4 is too far off. The distances in the bromide-disilicate are longer in general as can be seen regarding the mean distances.

Si_2O_7 -Groups

The second characteristic structural feature are two different disilicate groups formed by Si1 and Si2 with O11 as the bridging oxygen, and Si3 and Si4 with the bridging O3. The SiO_4 -tetrahedra are almost ideal with four Si–O bonds of similar length (mean Si–O distance: 1.621 Å). The Si–O–Si angles are 145.8° and 138.4° for the chloride and 146.3° and 140.8° for the bromide, respectively, with the two SiO_4 -tetrahedra in eclipsed configuration (Fig. 4).

DISCUSSION

Up to now only a limited number of compounds containing Cr^{2+} in an environment of oxygen or halogen atoms has been known. Table 7 gives a summary. Generally, these compounds exhibit a 4 + 2 coordination for Cr^{2+} (4 shorter bonds to ligands in a square planar arrangement and two longer bonds to ligands above and below the plane). Due to the Jahn–Teller effect a stabilization of the d^4 electron configuration of Cr^{2+} is achieved in such ligand fields of symmetry lower than O_h . The variety of coordination polyhedra observed for Cr^{2+} in the disilicate-dihalides gives striking evidence for this stereochemical effect. Comparison of the mixed ligand environments around Cr^{2+} shows that there seems to be a tendency to form four short (strong) bonds to oxygen in a square-planar arrangement,

TABLE 3

Atomic Positions and Isotropic Displacement Parameters of $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$, (Pc , $Z = 4$, $a = 6.414(3)$ Å, $b = 12.829(6)$ Å, $c = 10.540(6)$ Å, $\beta = 91.61(4)^\circ$)

Atom	x	y	z	U_{eq}
Cr1	0.1947(4)	0.1288(2)	0.4017(2)	0.0147(4)
Cr2	0.8147(4)	0.0380(2)	0.5876(3)	0.0196(5)
Cr3	0.8203(3)	0.7212(2)	0.5776(2)	0.0171(4)
Cr4	0.2168(3)	0.6285(2)	0.8852(2)	0.0144(4)
Cr5	0.1845(4)	0.3619(2)	0.8821(2)	0.0190(5)
Cr6	0.1583(4)	0.8870(2)	0.4080(2)	0.0173(5)
Cr7	0.5479(3)	0.7695(2)	0.0806(2)	0.0160(4)
Cr8	0.5587(4)	0.5448(2)	0.6831(2)	0.0167(4)
Si1	0.0667(6)	0.5054(3)	0.6268(3)	0.0137(7)
Si2	0.0587(5)	0.7398(3)	0.1462(3)	0.0130(7)
Si3	0.3216(6)	0.9992(3)	0.6459(3)	0.0122(7)
Si4	0.3252(6)	0.7610(3)	0.6377(3)	0.0127(7)
O1	0.127(1)	0.0234(7)	0.5441(9)	0.014(2)
O2	0.254(2)	0.0005(8)	0.791(1)	0.021(2)
O3	0.378(2)	0.8814(7)	0.6031(9)	0.015(2)
O4	0.250(2)	0.5459(7)	0.7240(9)	0.016(2)
O5	0.254(2)	0.7561(7)	0.7805(9)	0.018(2)
O6	0.509(1)	0.0741(7)	0.6117(9)	0.016(2)
O7	0.228(2)	0.7273(7)	0.0315(9)	0.014(2)
O8	-0.139(1)	0.5743(7)	0.6439(9)	0.015(2)
O9	0.169(2)	0.7743(7)	0.2789(9)	0.016(2)
O10	0.130(1)	0.7351(7)	0.5365(9)	0.016(2)
O11	0.024(2)	0.3845(7)	0.675(1)	0.018(2)
O12	0.150(2)	0.5040(7)	0.4839(9)	0.015(2)
O13	-0.147(1)	0.8042(7)	0.1103(9)	0.017(2)
O14	0.521(1)	0.6885(7)	0.6057(9)	0.017(2)
Br1	-0.2590(2)	0.8785(1)	0.4286(1)	0.0181(3)
Br2	0.6486(2)	0.6127(1)	-0.0527(1)	0.0234(3)
Br3	0.5821(2)	0.3675(1)	0.7952(1)	0.0198(3)
Br4	-0.2003(2)	0.1246(1)	0.2789(2)	0.0238(3)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j$$

Note. Standard deviations in parentheses.

TABLE 4
Interatomic Distances [Å] and Angles (°) for Cr₄(Si₂O₇)Cl₂

Cr1	O5	O2	O1	O7	Cl4	
O5	1.981	3.111	4.043	2.613	3.238	
O2	101.15	2.046	2.781	4.083	3.179	
O1	173.10	84.99	2.070	3.034	3.598	
O7	79.69	160.62	93.47	2.096	4.069	
Cl4	86.47	83.24	97.48	116.08	2.686	
Cr2	O6	O13	O1	Cl1	Cl4	
O6	2.031	2.632	4.072	3.528	3.524	
O13	80.48	2.043	2.894	4.448	4.311	
O1	167.21	89.55	2.066	3.158	3.643	
Cl1	99.31	148.61	85.01	2.575	3.498	
Cl4	94.47	128.86	98.03	82.53	2.726	
Cr3	O14	O8	O10	Cl1	Cl4	
O14	2.010	2.613	4.061	3.385	3.517	
O8	80.78	2.022	2.945	4.444	4.095	
O10	170.86	92.24	2.063	3.131	3.764	
Cl1	98.08	166.07	87.26	2.455	3.498	
Cl4	90.24	112.26	97.90	81.57	2.877	
Cr4	O5	O4	O12	O7	Cl2	
O5	1.990	2.831	4.015	2.613	3.456	
O4	90.09	2.011	2.807	4.109	3.417	
O12	174.20	88.02	2.030	3.257	3.422	
O7	78.80	167.24	103.64	2.124	3.211	
Cl2	93.84	91.95	91.71	82.64	2.695	
Cr5	O12	O9	O10	Cl3	O11	O4
O12	2.016	4.042	2.971	3.812	3.695	2.807
O9	164.75	2.062	2.720	3.177	2.512	3.992
O10	93.05	82.13	2.078	4.126	4.132	4.752
Cl3	110.00	84.60	122.55	2.618	3.851	3.027
O11	107.60	65.07	126.33	96.43	2.546	2.567
O4	70.85	112.31	163.34	69.00	58.19	2.724
Cr6	O9	O2	O1	O10	O3	Cl1
O9	1.977	2.923	4.189	2.720	3.850	3.491
O2	94.51	2.003	2.781	4.288	3.680	3.927
O1	176.74	82.35	2.213	3.615	2.525	3.158
O10	77.86	163.49	105.40	2.330	2.553	3.131
O3	117.80	108.85	64.32	63.60	2.508	4.357
Cl1	98.88	117.04	81.84	78.88	117.49	2.588
Cr7	O13	O6	O7	Cl2	Cl3	
O13	2.015	2.632	4.130	3.234	3.465	
O6	81.22	2.028	2.994	4.334	4.209	
O7	170.96	92.16	2.127	3.211	3.818	
Cl2	93.56	155.48	89.95	2.407	3.565	
Cl3	89.28	118.57	99.33	85.09	2.844	
Cr8	O14	O8	O4	Cl3	Cl2	Cl2
O14	2.029	2.613	2.881	4.453	3.779	4.185
O8	80.05	2.033	4.054	3.544	3.623	3.452
O4	90.20	169.27	2.038	3.027	3.417	4.285
Cl3	175.07	104.87	84.87	2.427	3.538	3.565
Cl2	97.61	91.93	84.88	82.08	2.931	5.978
Cl2	104.17	79.20	107.79	77.34	154.54	3.197
Si1	O8	O12	O11	O4		
O8	1.606	2.716	2.628	2.661		
O12	114.82	1.618	2.653	2.649		
O11	108.30	109.50	1.630	2.567		
O4	110.57	109.22	103.85	1.631		
Si2	O13	O9	O11	O7		
O13	1.601	2.702	2.692	2.671		
O9	114.75	1.608	2.512	2.651		
O11	113.29	102.08	1.623	2.628		
O7	110.46	108.87	106.82	1.651		
Si3	O2	O6	O3	O1		
O2	1.602	2.730	2.652	2.717		
O6	116.62	1.606	2.611	2.654		
O3	110.47	107.76	1.626	2.525		
O1	112.33	108.26	100.04	1.669		
Si4	O5	O14	O3	O10		
O5	1.598	2.693	2.615	2.698		
O14	114.33	1.607	2.631	2.662		
O3	108.53	109.13	1.623	2.553		
O10	112.20	109.50	102.44	1.652		
$\varphi(\text{Si1-O11-Si2})$				145.79		
$\varphi(\text{Si3-O3-Si4})$				138.44		

Note. Highest estimated standard deviations (SHELXL-93): distances Cr–O: 0.002 Å, Cr–Cl: 0.001 Å, Si–O: 0.002 Å, angles O–O: 0.11°, O–Cl: 0.06°, O–Si–O: 0.13°.

TABLE 5
Interatomic Distances [\AA] and Angles ($^\circ$) for $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$

Cr1	O5	O2	O1	O7	Br4	
O5	1.995	3.138	4.064	2.657	3.289	
O2	101.11	2.068	2.826	4.125	3.327	
O1	172.90	85.99	2.076	3.018	3.683	
O7	80.74	162.65	92.39	2.105	4.115	
Br4	84.51	84.50	96.62	112.84	2.812	
Cr2	O6	O13	O1	Br1	Br4	
O6	2.037	2.703	4.096	3.520	3.590	
O13	82.76	2.052	2.920	4.547	4.494	
O1	170.41	90.10	2.074	3.300	3.796	
Br1	95.62	147.66	86.97	2.678	3.701	
Br4	91.49	129.31	98.00	82.94	2.904	
Cr3	O14	O8	O10	Br1	Br4	
O14	1.995	2.647	4.036	3.401	3.478	
O8	82.36	2.025	2.937	4.569	4.140	
O10	172.03	92.20	2.052	3.277	3.815	
Br1	94.62	162.29	88.80	2.599	3.701	
Br4	88.37	112.95	99.14	84.29	2.906	
Cr4	O5	O4	O12	O7	Br2	
O5	1.992	2.762	4.032	2.657	3.556	
O4	87.04	2.018	2.902	4.150	3.533	
O12	174.18	91.19	2.045	3.299	3.564	
O7	79.26	164.90	103.06	2.168	3.342	
Br2	93.23	91.85	92.37	82.68	2.835	
Cr5	O12	O9	O10	Br3	O11	O4
O12	2.044	4.090	3.020	3.831	3.629	2.902
O9	170.92	2.059	2.780	3.216	2.481	4.183
O10	93.96	84.20	2.087	4.127	4.148	4.958
Br3	105.70	82.97	117.11	2.735	3.768	3.203
O11	109.01	66.99	134.73	94.06	2.406	2.570
O4	68.86	112.93	162.78	68.82	56.63	2.926
Cr6	O9	O2	Br1	O1	O10	O3
O9	1.988	2.942	3.471	4.259	2.780	3.886
O2	94.99	2.004	3.951	2.826	4.351	3.684
Br1	94.51	113.71	2.694	3.300	3.277	4.432
O1	175.05	82.40	82.76	2.275	3.699	2.498
O10	78.40	165.30	80.15	105.09	2.383	2.546
O3	121.42	110.80	118.55	63.52	63.39	2.460
Cr7	O13	Br2	O6	O7	Br3	
O13	2.023	3.253	2.703	4.134	3.444	
Br2	90.00	2.548	4.477	3.342	3.712	
O6	83.17	153.57	2.049	3.021	4.251	
O7	172.92	91.00	92.87	2.119	3.832	
Br3	87.73	86.32	118.72	99.32	2.868	
Cr8	O14	O8	O4	Br3	Br2	Br2
O14	2.028	2.647	2.838	4.589	3.796	4.296
O8	81.46	2.028	4.049	3.597	3.544	3.426
O4	88.48	168.82	2.040	3.203	3.533	4.428
Br3	174.96	102.45	87.34	2.565	3.551	3.712
Br2	97.39	88.54	87.93	79.66	2.959	6.011
Br2	106.12	76.72	111.02	78.05	149.79	3.266
Si1	O8	O12	O4	O11		
O8	1.604	2.696	2.636	2.668		
O12	113.98	1.611	2.648	2.671		
O4	109.62	109.98	1.622	2.570		
O11	109.85	109.64	103.23	1.656		
Si2	O13	O9	O11	O7		
O13	1.593	2.684	2.736	2.670		
O9	113.75	1.611	2.481	2.669		
O11	115.75	99.56	1.638	2.638		
O7	110.73	109.73	106.60	1.652		
Si3	O6	O2	O3	O1		
O6	1.589	2.706	2.612	2.617		
O2	115.86	1.604	2.643	2.725		
O3	108.96	110.15	1.620	2.498		
O1	107.60	113.52	99.45	1.654		
Si4	O5	O14	O3	O10		
O5	1.587	2.696	2.608	2.684		
O14	115.14	1.607	2.641	2.662		
O3	108.53	109.57	1.625	2.546		
O10	111.66	109.34	101.75	1.656		
$\varphi(\text{Si1-O11-Si2})$				146.25		
$\varphi(\text{Si3-O3-Si4})$				140.78		

Note. Highest estimated standard deviations (SHELXL-93): distances Cr–O: 0.011 \AA , Cr–Br: 0.003 \AA , Si–O: 0.011 \AA , angles O–O: 0.56 $^\circ$, O–Br: 0.32 $^\circ$, O–Si–O: 0.72 $^\circ$.

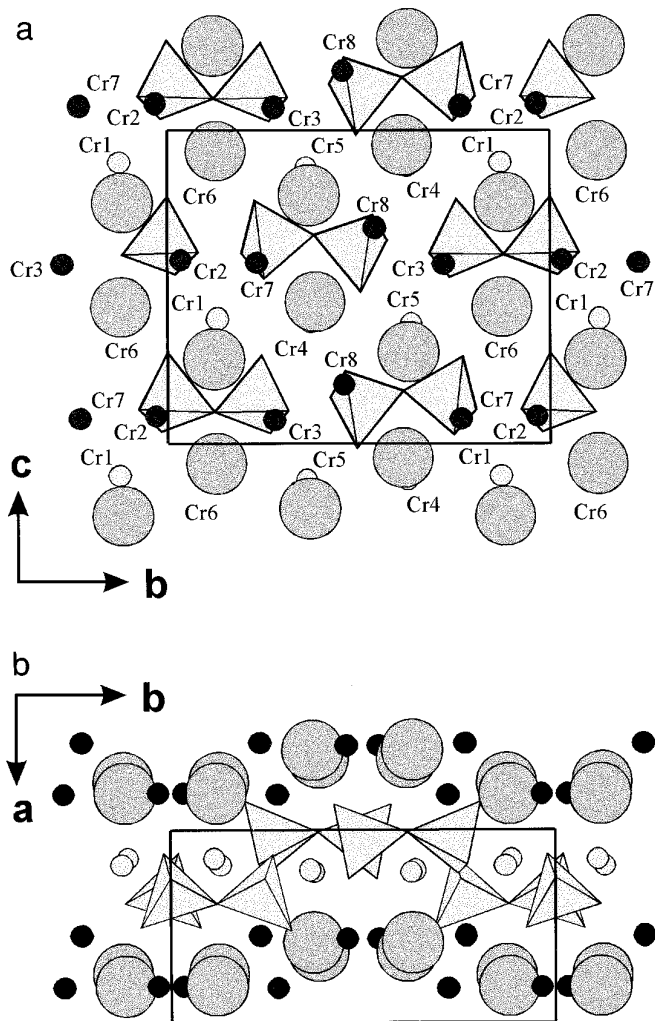


FIG. 1. ATOMS-plots (18) of $\text{Cr}_4(\text{Si}_2\text{O}_7)_2\text{Cl}_2$. Small circles represent Cr^{2+} (group 1 (Cr1, Cr4, Cr5, Cr6) light gray, group 2 (Cr2, Cr3, Cr7, Cr8) dark gray), large circles represent chloride. The Si_2O_7 -groups are shown as polyhedra. (a) Projection along the *a*-axis with slightly warped hexagonal nets parallel to (1 0 0) formed by chloride. (b) Projection along *c* emphasizing the "chromous-disilicate" and the "chromous-dichloride" substructure. While the chromium ions coordinated mainly by oxygen are sited in a layer between the disilicate groups, the Cr^{2+} coordinated by more halogen are in a row with the halogen atoms.

while halide ions prefer axial ligand positions with longer (weaker) bonds.

This generalization leads to interesting aspects in the discussion of the structure. Due to the difference in size of O^{2-} , Cl^- , and Br^- , assignment of coordination numbers to Cr^{2+} becomes rather arbitrary on the basis of simple bond distances. For the five Cr atoms coordinated by only five ligands, for example, another oxygen or halogen atom is found within the range of 3.0–3.8 Å.

In order to rationalize the suggested structure model and to compare observed interatomic distances with those

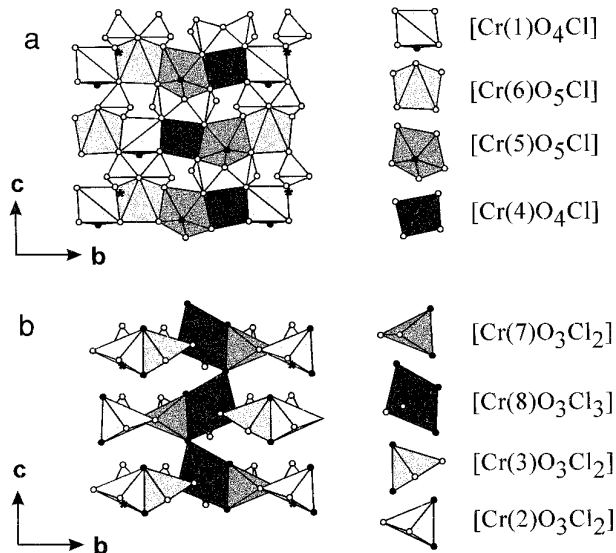


FIG. 2. ATOMS-plots (18) of $\text{Cr}_4(\text{Si}_2\text{O}_7)_2\text{Cl}_2$ visualizing the connectivity of the $[\text{CrO}_x\text{Cl}_y]$ polyhedra. Projection along *a*. (a) Coordination polyhedra around Cr ions of group 1. (b) Coordination polyhedra around Cr ions of group 2. Open circles at the vertices of the polyhedra indicate oxygen, filled circles represent chlorine.

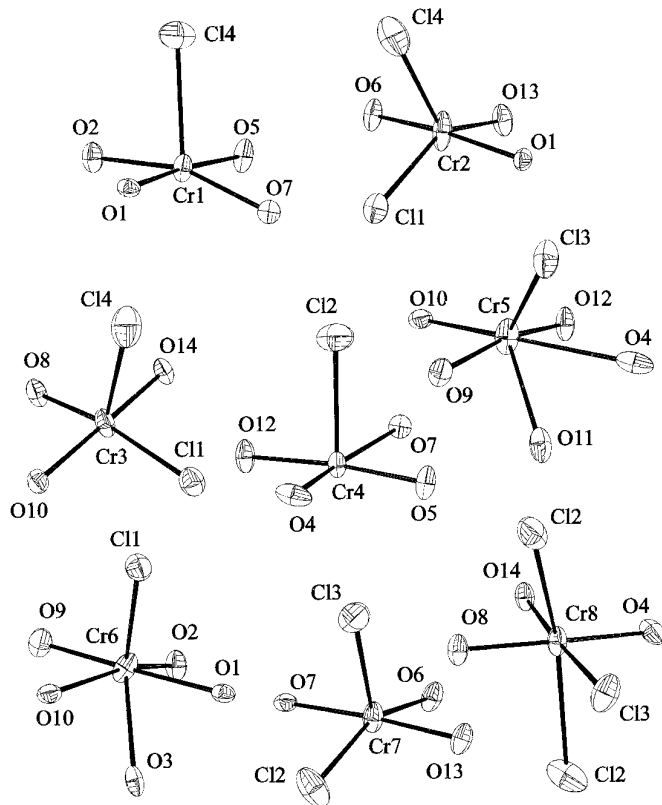


FIG. 3. ORTEP-plots (17) of the coordination polyhedra around Cr^{2+} ions in $\text{Cr}_4(\text{Si}_2\text{O}_7)_2\text{Cl}_2$. Ellipsoids with 88% probability are displayed.

TABLE 6
Connectivity Matrix, Partial Bond-Valences ν_i According to (19) and ECoN (21) for $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$

	O1	O2	O3	O4	O5	O6	O7	O8	O9	O10	O11	O12	O13	O14	Cl1	Cl2	Cl3	Cl4	$\Sigma \nu_i$	ECoN	C.N.
Cr1	0.399	0.426			0.507		0.372											0.200	1.904	4.659	5
Cr2	0.403					0.443							0.429		0.270			0.179	1.724	4.612	5
Cr3								0.454		0.407				0.469	0.373			0.119	1.824	4.325	5
Cr4				0.468	0.495		0.345					0.444				0.195			1.950	4.592	5
Cr5				0.068					0.408	0.390	0.110	0.462					0.240		1.678	4.138	6
Cr6	0.271	0.478	0.122						0.513	0.198					0.260				1.842	4.690	6
Cr7						0.447	0.342						0.463			0.425	0.130		1.807	4.368	5
Cr8				0.435				0.441						0.446	0.103	0.050	0.402		1.877	4.292	6
Si1				0.981				1.050			0.984	1.016							4.031	3.995	4
Si2							0.930		1.044	1.003		1.064							4.041	3.982	4
Si3	0.885	1.061	0.995			1.050													3.991	3.966	4
Si4			1.003		1.073					0.927				1.047					4.050	3.979	4
$\Sigma \nu_i$	1.961	1.961	2.112	1.951	2.072	1.940	1.989	1.942	1.964	1.921	2.091	1.929	1.957	1.960	0.903	0.770	0.772	0.500			
ECoN	3.899	2.992	2.248	3.019	2.996	3.000	3.987	2.999	2.970	3.683	2.187	2.998	2.996	2.999	2.943	2.527	2.601	3.043			
C.N.	4	3	3	3	3	3	4	3	3	4	3	3	3	3	3	4	3	3			

of already known crystal structures containing Cr^{2+} , we applied bond-length bond-strength considerations (19, 20) as well as the ECoN concept developed by Hoppe (21).

According to Brese and O'Keeffe (19) the valence ν_{ij} associated with a given distance d_{ij} between atoms i and j is expressed by Eq. [3]. All individual valences ν_{ij} for atom i and the ligands j add up to the total valence V_i of an atom i (Eq. [4]).

$$\nu_{ij} = e^{(R_{ij}-d_{ij})/b} \quad [3]$$

$$\sum \nu_{ij} = V_i. \quad [4]$$

R_{ij} , the bond-distance (in Å) corresponding to unit valence, is listed for many combinations of cations and anions in (19) ($R_{\text{Cr(II)}-\text{O}} = 1.73$, $R_{\text{Cr(II)}-\text{Cl}} = 2.09$, $R_{\text{Cr(II)}-\text{Br}} = 2.26$, $R_{\text{Si(IV)}-\text{O}} = 1.624$). b is an empirically found constant of the value 0.37 Å. With Eq. [3] and the appropriate R_{ij} we estimated the contribution of the individual bonds to the total valence of the different atoms in $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ and $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$. The results are given for the chloride-disilicate in Table 6. Those for the bromide-disilicate are very similar and are therefore omitted. The total valences found for Si^{4+} are very close to 4. V_i found for Cr^{2+} are significantly lower ($1.68 \leq V_i(\text{Cr}) \leq 1.95$) than the expected value of 2 and show great variation. For most oxygen atoms $V_i = 1.95 \pm 0.03$ is found, with the exception of O5 and the bridging oxygen atoms of the disilicate groups (O3, O11) having $V_i = 2.10 \pm 0.01$. While the "hyper-valence" of O3 and O11 is in agreement with values found in other disilicates, the rather high V_i for O5 is not understandable from structural reasons. Even worse is the agreement between observed and expected valences for the halide ions: 0.90 (Cl1), 0.77 (Cl2), 0.77 (Cl3), 0.50 (Cl4). Therefore, we applied the ECoN (effective coordination

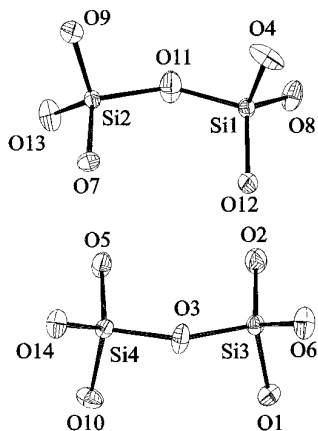


FIG. 4. ORTEP-plots (17) of the disilicate groups in $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$. Ellipsoids with 88% probability are displayed.

TABLE 7
 Coordination Geometry around Cr^{2+} , MAPLE (22) and MAPLE (“CrO”) Values for oxo-Compounds, oxo-Halides and Halides of Divalent Chromium

Compound/color	Coordination geometry	MAPLE (kcal/mol) compound	MAPLE (kcal/mol) “CrO” ^a	Reference
$\text{Cr}_2^+\text{Cr}_4^{3+}(\text{P}_2\text{O}_7)_4$ yellowish-green	$d(\text{Cr}-\text{O}(\text{short}))$: 1.96, 2.02, 2.05, $d(\text{Cr}-\text{O}(\text{long}))$: 2.15 Å 2.60, 2.64 Å	53149.8	1129.1	(5)
$\text{Cr}_3^+\text{Cr}_4^{3+}(\text{PO}_4)_6$ brown-transparent	$d(\text{Cr}(2)-\text{O})$: ^b 2.02 (2x), 2.26 (2x), 2.33 (2x) Å $d(\text{Cr}(4)-\text{O})$: ^b 2.03, 2.05, 2.05, 2.16, 2.21 Å	43668.9	1129.9	(6)
Cr_2SiO_4 magenta	$d(\text{Cr}-\text{O}(\text{short}))$: 2.05 Å (4x) $d(\text{Cr}-\text{O}(\text{long}))$: 2.72 Å (2x)	5711.7	1046.5	(7)
$\text{CaCrSi}_4\text{O}_{10}$ red	$d(\text{Cr}-\text{O})$: 2.00 Å (4x)	16688.0	1095.8	(4)
$\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$ deep-blue	mean $d(\text{Cr}-\text{O}(\text{short}))$: 2.047 Å mean $d(\text{Cr}-\text{O}(\text{long}))$: 2.381 Å mean $d(\text{Cr}-\text{Cl})$: 2.798 Å	11111.2	1078.9	this work
$\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ deep-blue	mean $d(\text{Cr}-\text{O}(\text{short}))$: 2.039 Å mean $d(\text{Cr}-\text{O}(\text{long}))$: 2.464 Å mean $d(\text{Cr}-\text{Cl})$: 2.694 Å	11129.1	1060.9	this work
$\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ turquoise	$d(\text{Cr}-\text{O})$: 2.05 Å (4x) $d(\text{Cr}-\text{Cl})$: 3.03 Å (2x)	21364.7	1036.1	(2)
$\text{Cr}_3\text{B}_7\text{O}_{13}\text{Br}$ blue-turquoise	$d(\text{Cr}-\text{O})$: 2.06 Å (4x) $d(\text{Cr}-\text{Br})$: 3.04 Å (2x)	21319.1	1032.2	(3)
$\text{Cr}_3\text{B}_7\text{O}_{13}\text{I}$ green-turquoise	$d(\text{Cr}-\text{O})$: 2.08 Å (4x) $d(\text{Cr}-\text{I})$: 3.05 Å (2x)	21242.2	1010.3	(1)
CrCl_2 grayish	$d(\text{Cr}-\text{Cl})$: 2.39 Å (4x) $d(\text{Cr}-\text{Cl})$: 2.91 Å (2x)	625.9	—	(24)
CrBr_2 grayish	$d(\text{Cr}-\text{Br})$: 2.55 Å (4x) $d(\text{Cr}-\text{Br})$: 3.00 Å (2x)	554.1	—	(25)
CrI_2 brown	$d(\text{Cr}-\text{I})$: 2.74 Å (4x) $d(\text{Cr}-\text{I})$: 3.23 Å (2x)	510.20	—	(25)
$\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$ blue	$d(\text{Cr}-\text{O})$: 2.08 Å (4x) $d(\text{Cr}-\text{Cl})$: 2.76 Å (2x)	—	—	(26)

^a The MAPLE (22) increment for the “CrO” have been determined from the MAPLE value of the respective compound minus the oxides contained besides “CrO.” The value for B_2O_3 in the B_7O_{13} -group was determined from $\text{Mg}_3\text{B}_7\text{O}_{13}$ (27), the value for SiO_2 of the Si_4O_{10} -group was determined from $\text{CaCuSi}_4\text{O}_{10}$ (28), SiO_2 in Si_2O_7 from BaVSi_2O_7 (29), P_2O_5 in P_2O_7 from $\text{Na}_2\text{P}_2\text{O}_7$ (5), P_2O_5 in PO_4 average from several orthophosphates (10650 kcal/mol), SiO_2 in SiO_4 from MgCaSiO_4 (27). Oxides from (27).

^b Numbers of the different Cr^{2+} refer to the numbers given in Ref. (6).

numbers) concept, introduced by Hoppe (21). For comparison, ECoN as well as c.n. from bond-length bond-strength considerations are also included in Table 6 for all atoms. Again, for Si coordinations close to the ideal value of 4 are found, while for all other atoms more or less pronounced deviations from ideal coordination numbers result. This leads us to the conclusion that both concepts are unable to reproduce the particular bonding situation in compounds like $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Cl}_2$ and $\text{Cr}_4(\text{Si}_2\text{O}_7)\text{Br}_2$, where a wide range of interatomic distances is observed within one coordination polyhedron due to different ligand types and the Jahn–Teller-effect.

Table 7 gives the *M*adelung *P*arts of *L*attice *E*nergy (MAPLE (22)) of a number of compounds containing Cr^{2+} .

Even though the coordination geometry around Cr^{2+} varies remarkably for the different oxo- and oxo-halide-compounds, the increment MAPLE(“CrO”) derived from the data shows much less variation. The values are in the range 1010–1130 kcal/mol confirming similar bonding behavior of Cr^{2+} in all compounds.

The halide-disilicates have a deep-blue color, while most other chromous compounds mentioned in Table 7, like $\text{Cr}_3(\text{B}_7\text{O}_{13})X$ ($X = \text{Cl}, \text{Br}, \text{I}$) (1–3) and the diphosphate $\text{Cr}_2\text{P}_2\text{O}_7$ (23), show less intensive blueish colors. This observation is in accordance with the highly distorted coordination polyhedra around Cr^{2+} lacking a center of symmetry. In contrast to this $\text{CaCrSi}_4\text{O}_{10}$ (4) is red with a square planar coordination of the Cr^{2+} ions.

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