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The Crystal Structure and Composition of Yedlinite

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Abstract

The crystal structure of the new mineral yedlinite has been determined using the Patterson method and refined to $R = 0.14$. The structure indicates the composition to be $Pb_6Cl_6CrX_6Y_2$ where X is O^{2-} or OH^-, and Y is O^{2-}, OH^-, or H_2O. The structure contains a continuous three-dimensional framework of irregular $Pb(Cl_5X_2Y)$ polyhedra and CrX octahedra. Chromium seems to be in the 6+ valence state, and the structure of yedlinite appears to contain the first recognized occurrence of an octahedrally coordinated Cr^{6+} ion.

Introduction

Several small crystals of yedlinite, a new mineral from the Mammoth Mine, Tiger, Arizona, were obtained from U.S. National Museum Specimen R-8171 for a study of the crystal structure. Yedlinite has been described by McLean, Bideaux, and Thomssen (1974) who report crystallographic data as follows: $a = 12.868$, $c = 9.821$ Å, space group = $R\bar{3}$, $Z = 3$, density (obs) = 5.85 gm/cc.

The chemical composition of yedlinite was in doubt at the inception of the structure study because determination of oxygen, hydroxyl, and water and of the valence of chromium could not be made from the chemical analysis. The elucidation of the structural formula of yedlinite was expected to be a contribution of the investigation.

Experimental

The process of preparing a sphere of the mineral for data collection was complicated by a distinct prismatic cleavage and a lack of brittleness. Intensity data were finally obtained using a very small spheroid of mean diameter about 0.045 mm and absorption coefficient, μR, 1.36 for Mo radiation. Data were collected on an automated Picker diffractometer using monochromatized Mo radiation, and intensities less than 2σ were considered unobserved. Both $\bar{h}kil$ and $hkil$ portions of the reflection sphere were collected and corrected for the usual geometrical factors. Approximate absorption corrections were applied using the spherical correction factors from pages 302–305 of Vol. 2 of the *International Tables for X-Ray Crystallography*. The structure factor values of symmetrically equivalent reflections within the data set were averaged. A general agreement of structure factors from equivalent planes increased confidence in much of the data, but systematic differences for a number of equivalent reflections, with $\bar{h}kil$ generally having greater F than the equivalent $hkil$ reflection, gave evidence of sig-

TABLE 1. Position and Temperature Parameters in Yedlinite*

Atom	x	y	z	B
Pb	.1829(5)*	.1379(5)	.2121(5)	2.27(14)
Cl	.0869(31)	.2886(30)	.1050(37)	2.14(68)
Cr	.0000	.0000	.5000	.60(77)
X**	.133(8)	.091(8)	.604(9)	2.1(1.8)
Y**	.0000	.0000	.108(16)	3.6(3.2)

* Numbers in parentheses are estimated standard deviations and refer to the last places.

** X=O^{2-} or OH^-; Y=O^{2-}, OH^-, or H_2O

nificant uncorrected absorption error. No attempt was made to correct for the trend except through the averaging process. Only 290 observed structure factors were recorded. The weakness of the diffraction spectrum can be attributed to the very small crystal size, the substantial absorption of the crystal, and the soft and non-brittle nature of the mineral which promotes structure damage to the surficial parts of the crystal during grinding. Crystals after grinding gave notably weaker diffraction results than unground crystals of similar size. Because of the dearth of material, it seemed unlikely that a better sphere could be obtained. Attempts to collect data on unground crystal fragments proved unsatisfactory and were abandoned.

TABLE 2. Observed and Calculated Structure Factors for Yedlinite*

h	k	l	FO	FC	h	k	l	FO	FC	h	k	l	FO	FC
3	0	0	369	-324	2	0	2	121	45	1	0	4	183	224
6	0	0	335	293	5	0	2	72	-19	4	0	4	349	-348
9	0	0	235	-209	8	0	2	339	320	7	0	4	148	128
1	1	0	288	265	0	1	2	169	-515	10	0	4	328	-316
4	1	0	360	-325	3	1	2	838	858	2	1	4	528	-571
7	1	0	171	-158	9	1	2	127	143	5	1	4	117	98
2	2	0	286	-260	1	2	2	334	368	8	1	4	106	-122
5	2	0	181	-199	4	2	2	297	305	0	2	4	122	269
8	2	0	142	116	7	2	2	55	-31	3	2	4	372	-389
3	3	0	128	106	10	2	2	113	-102	6	2	4	184	184
6	3	0	195	-162	2	3	2	181	155	1	3	4	160	-171
9	3	0	381	347	5	3	2	92	82	4	3	4	178	198
1	4	0	454	413	8	3	2	364	-358	7	3	4	155	175
4	4	0	45	12	0	4	2	107	-90	2	4	4	268	272
7	4	0	350	322	3	4	2	436	-415	8	4	4	198	191
2	5	0	806	738	6	4	2	67	79	0	5	4	256	241
5	5	0	207	-183	9	4	2	161	-163	3	5	4	54	89
8	5	0	168	171	1	5	2	488	-472	6	5	4	157	-166
3	6	0	169	161	4	5	2	242	242	1	6	4	311	327
1	7	0	166	169	2	6	2	274	-258	4	6	4	421	-416
4	7	0	211	-171	5	6	2	351	336	5	7	4	171	-187
2	8	0	197	-148	3	7	2	327	285	1	9	4	175	192
3	9	0	242	234	1	8	2	55	1	2	10	4	115	138
					3	10	2	295	-272					
1	0	1	79	156						2	0	5	92	109
4	0	1	475	433	0	0	3	822	-730	5	0	5	187	142
7	0	1	117	-80	3	0	3	286	-253	0	1	5	156	418
10	0	1	305	262	6	0	3	209	-204	3	1	5	92	-120
2	1	1	370	373	9	0	3	151	-124	6	1	5	338	-320
5	1	1	191	-181	1	1	3	193	-352	1	2	5	174	-189
8	1	1	67	63	4	1	3	140	-96	4	2	5	162	-216
11	1	1	226	-221	7	1	3	262	239	7	2	5	208	-187
0	2	1	270	-296	2	2	3	302	-302	2	3	5	83	-8
3	2	1	438	430	5	2	3	444	428	5	3	5	409	-395
6	2	1	570	-535	8	2	3	170	-140	8	3	5	270	266
9	2	1	119	94	0	3	3	470	588	0	4	5	280	-336
1	3	1	122	86	3	3	3	212	-226	3	4	5	204	270
4	3	1	450	-419	6	3	3	358	343	1	5	5	395	435
7	3	1	67	-134	9	3	3	172	-177	2	6	5	202	211
2	4	1	154	131	1	4	3	173	-171	3	7	5	82	-93
5	4	1	174	-167	4	4	3	114	87	1	8	5	259	-239
8	4	1	72	109	7	4	3	253	-213	0	10	5	261	-288
0	5	1	123	-114	2	5	3	437	-425					
3	5	1	52	89	0	6	3	259	-197	0	0	6	205	-178
6	5	1	236	198	3	6	3	182	-198	3	0	6	380	407
1	6	1	155	110	6	6	3	72	-60	9	0	6	349	319
4	6	1	302	292	4	7	3	144	-176	1	1	6	109	184
7	6	1	84	-138	2	8	3	294	256	4	1	6	275	289
2	7	1	75	-89	0	9	3	391	360	7	1	6	81	-114
0	8	1	365	-360	3	9	3	72	-127	2	2	6	371	433
1	9	1	475	-438	1	10	3	133	155	5	2	6	329	-328

* Scale factor is 1.287.

TABLE 2, Continued

h	k	l	FO	FC	h	k	l	FO	FC	h	k	l	FO	FC
0	3	6	168	-277	-4	6	2	529	-446	-6	9	6	150	-186
3	3	6	66	105	-3	7	2	304	284	-5	10	6	111	-137
6	3	6	194	-205	-6	7	2	576	-475	-8	10	6	190	186
1	4	6	75	-75	-5	8	2	276	-224	-7	11	6	209	-231
4	4	6	69	-84	-4	9	2	185	176	-5	6	7	322	-351
5	5	6	249	231	-7	9	2	150	115	-4	7	7	269	-312
4	7	6	311	318	-9	10	2	409	351	-3	8	7	167	181
0	9	6	248	-230	-2	11	2	232	-182	-6	8	7	268	-249
					-4	12	2	349	-293	-8	9	7	114	104
1	0	7	379	-402	-9	13	2	159	-180	-5	7	9	210	244
4	0	7	112	102										
2	1	7	256	272	-4	5	3	371	-330	-2	10	0	124	116
3	2	7	147	157	-3	6	3	69	33	-2	9	1	195	201
6	2	7	144	138	-5	7	3	538	-452	-2	9	4	160	-171
1	3	7	85	77	-4	8	3	167	-111	-2	8	8	138	-175
2	4	7	296	-345	-7	8	3	184	-184	-2	8	5	170	-174
0	5	7	88	-159	-3	9	3	165	-181	-2	8	2	619	545
3	5	7	178	-196	-6	9	3	120	95	-2	7	0	235	-199
1	6	7	362	-395	-5	10	3	320	273	-2	7	3	260	-203
4	6	7	96	168	-4	11	3	148	-185	-2	7	6	378	372
0	8	7	94	122	-7	11	3	487	392	-2	7	9	140	-223
					-10	11	3	111	-102	-2	6	7	106	125
3	1	8	281	-321	-3	12	3	307	-283	-2	6	1	72	-56
6	1	8	275	263	-6	12	3	112	129	-2	5	2	108	-61
2	3	8	70	-102	-9	12	3	156	-154	-2	5	5	352	-387
5	3	8	330	319	-5	13	3	194	-145	-2	5	8	259	355
0	4	8	248	316						-2	4	6	268	-352
1	5	8	92	-126	-3	5	4	211	183	-2	4	3	569	587
					-5	6	4	375	341	-2	4	0	331	-261
0	0	9	339	392	-4	7	4	246	219	-2	3	1	312	-268
3	0	9	267	-255	-3	8	4	518	-476	-2	3	7	119	115
6	0	9	126	128	-6	8	4	151	141					
4	1	9	246	-245	-8	9	4	356	-313	-1	2	0	334	265
2	2	9	250	-263	-3	11	4	250	245	-1	2	3	103	97
1	4	9	110	139	-6	11	4	244	204	-1	3	8	161	337
2	5	9	227	238	-9	11	4	135	-114	-1	3	5	279	-424
					-8	12	4	114	127	-1	3	2	128	133
1	0	10	219	240						-1	4	1	986	-934
-3	5	1	203	-176	-3	4	5	288	-294	-1	4	4	337	352
-5	6	1	72	41	-4	6	5	385	346	-1	4	7	137	198
-4	7	1	234	167	-6	7	5	431	392	-1	4	10	179	-326
-3	8	1	484	402	-5	8	5	214	166	-1	7	4	397	-373
-6	8	1	79	79	-6	10	5	349	-303	-1	7	1	479	406
-5	9	1	299	-271	-2	11	5	160	136	-1	8	0	157	-158
-8	9	1	308	277	-4	12	5	238	232	-1	8	3	76	-77
-4	10	1	138	-78	-7	12	5	115	-162	-1	8	6	193	186
-7	10	1	320	-269						-1	9	5	180	-158
-6	11	1	502	-441	-4	5	6	76	20	-1	9	2	139	104
-8	12	1	111	-134	-4	8	6	212	149	-1	10	1	252	-222
					-7	8	6	108	104	-1	10	4	182	147
-3	4	2	323	269	-3	9	6	293	296	-1	12	2	158	206

Structure Determination and Refinement

Diffraction symmetry and systematic absences indicate the space group of yedlinite is either $R\bar{3}$ or $R3$. The structure was attempted in $R\bar{3}$ because the morphological symmetry of the crystals appears centric. Hexagonal axes were used throughout. A Patterson synthesis was used to locate the 18 lead atoms in a general position. This gave a conventional R factor of 0.21 after one cycle of full matrix least-squares refinement using a modified version of ORFLS (Busing, Martin, and Levy, 1962). The three chromium atoms were then located in a special position at $0,0,\frac{1}{2}$ from a Fourier difference map. Two additional occupied general positions were also detected, one with approximately twice the electron density of the other. The greater electron density was attributed to chlorine, and oxygen was assigned to

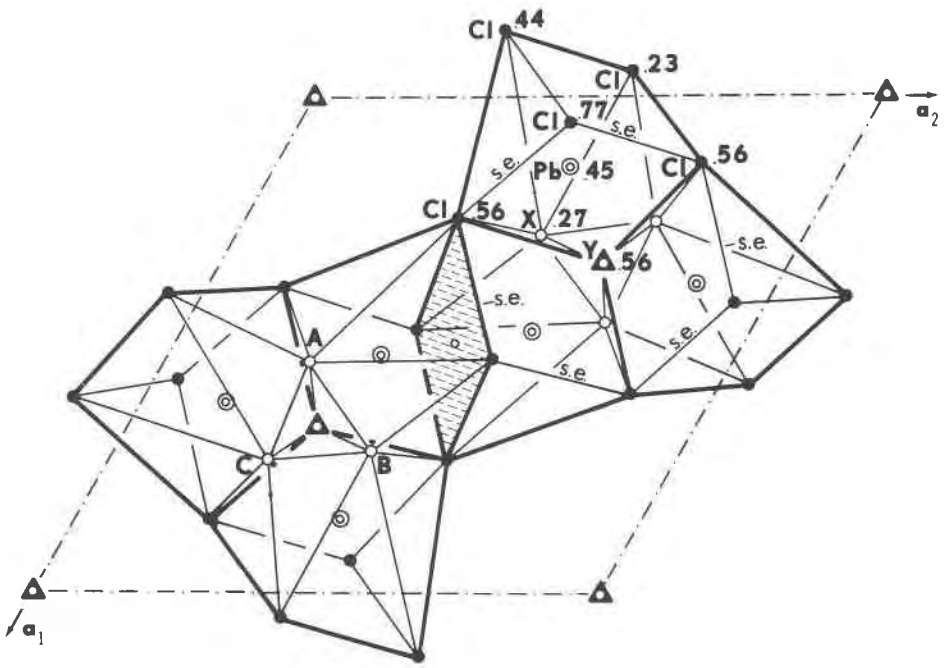

FIG. 1. A part of the structure of yedlinite viewed down the *c* axis. Shown are two pinwheels, each composed of three lead polyhedra. The linkage of the two adjacent pinwheels by face sharing (shaded face) is shown. Not explicitly shown are the pinwheels at the $\bar{3}$ axis passing through the cell origin and the linkage of center-of-symmetry related pinwheels along the $\bar{3}$ axes by sharing of Cl-Cl edges (**s.e.**) and through the Cr octahedron, one face of which is the equilateral triangle ABC.

the sites of lower electron density which were in octahedral coordination about the chromium atoms. Another Fourier difference map at this stage disclosed only the presence of oxygen-size peaks at a six-fold special position on the $\bar{3}$ axes. Additional least-squares refinement using isotropic temperature factors reduced *R* to 0.14, and subsequent difference maps failed to reveal significant electron density in the cell. Attempted refinements using anisotropic temperature factors reduced *R* to 0.11, but the temperature factors appeared unrealistic, presumably because of unresolved absorption error. Position and isotropic temperature parameters are shown in Table 1, and observed and calculated structure factors are in Table 2.

TABLE 3. Interatomic Distances and Angles in Yedlinite*

i	j	d_{ij}	i	j	d_{ij}	i	j	d_{ij}
Cr	X**	1.82(10)*	Pb	Cl	3.68(4)	Y	Y	2.12(32)
Pb	Cl	2.96(4)	Pb	Cl	4.41(4)	Y	X	3.20(13)
Pb	Cl	3.20(4)	Pb	X	2.70(10)			
Pb	Cl	3.33(4)	Pb	X	2.53(10)	Cl	Y	3.30(4)
Pb	Cl	3.38(4)	Pb	Y**	2.36(5)			

i	j	k	$Angle_{ijk}$	i	j	k	$Angle_{ijk}$
X	Cr	X	91.5(4.3)	X	Cr	X	88.5(4.3)

* Numbers in parentheses are estimated standard deviations and refer to the last places.

** X=O^{2-} or OH^-; Y=O^{2-}, OH^-, or H_2O

Crystal Chemistry

The crystal structure of yedlinite strongly endorses the chemical formula, $Pb_6Cl_6CrX_6Y_2$, where *X* and *Y* are the oxygen species, O, OH, or H_2O. Since charge equilibrium can be achieved in the formula by juggling the combinations of oxygen species in the *X* and *Y* sites coupled with variation of the valence of chromium from three to six, there are many possibilities consistent with the general formula. Several of the more likely that we have considered are:

with Cr^{3+}	with Cr^{6+}
$Pb_6Cl_6Cr(OH)_6(O, OH)_2$	$Pb_6Cl_6CrO_6 \cdot 2H_2O$
$Pb_6Cl_6Cr(O, OH)_6 \cdot 2H_2O$	$Pb_6Cl_6Cr(O, OH)_6(OH)_2$
$Pb_6Cl_6Cr(O, OH)_6(OH)_2$	$Pb_6Cl_6Cr(O, OH)_6(O, OH)_2$

The Cr-O interatomic distance in yedlinite (Table 3) is 1.82(10) Å. One would predict a Cr^{3+}-O dis-

tance of 2.00 Å, based on ionic radii for 6-fold coordination (Shannon and Prewitt, 1969), or about 1.98(8) Å from *International Tables for X-Ray Crystallography* (Vol. 3, 1968). A Cr^{6+}-O distance in 4-fold coordination would be 1.67 Å based both on the ionic radii of Shannon and Prewitt and the *International Tables*. A Cr^{6+}-O distance based on extrapolation of the values of Shannon and Prewitt would be about 1.81 Å for 6-fold coordination. The distance of 1.82 Å in yedlinite is consistent with a valence state of chromium of 6+, as is the occurrence of yedlinite in an oxidized assemblage.

Minimization of disorder favors the formula, $Pb_6Cl_6CrO_6 \cdot 2H_2O$. However, electrostatic neutrality of the oxygen sites is best achieved in $Pb_6Cl_6Cr(O,OH)_6(O,OH)_2$ where the *X* site deviates from neutrality by about 0.04 (not corrected for hydrogen bonding) and the *Y* site by about −0.10, well within normal limits. This, to our knowledge, would be the first recognized occurrence of Cr^{6+} in octahedral coordination. Minimal disorder and satisfactory oxygen site charge balance is achieved in $Pb_6Cl_6Cr(OH)_6(O,OH)_2$ with Cr^{3+} although a Cr^{3+}-O bond distance is not in as good agreement with the observed Cr-O distance. A refinement of the structure to resolve these variances is impractical until a satisfactory crystal for data collection can be prepared.

Discussion of the Structure

The most pervasive and continuous part of the structure of yedlinite is the coordination framework around the lead atoms. The bond distance and angle information in Table 3 shows that lead is coordinated by two *X* oxygen atoms, one *Y* oxygen atom, and five chlorine atoms, forming an irregular polyhedron. A sixth chlorine at a distance of 4.41 Å is not included in the coordinating group, as bonding would be minimal at that distance.

Three symmetry-related lead polyhedra share faces—each face consisting of one chlorine, one *X* oxygen, and one *Y* oxygen—to form a planar three member "pinwheel" centered on a $\bar{3}$ axis (Fig. 1). Each pinwheel shares six Cl-Cl edges (e.g., **s.e.** in Fig. 1) with the centrosymmetrically related pinwheel above or below on this $\bar{3}$ axis. These double pinwheel groups are linked to form stacks parallel to

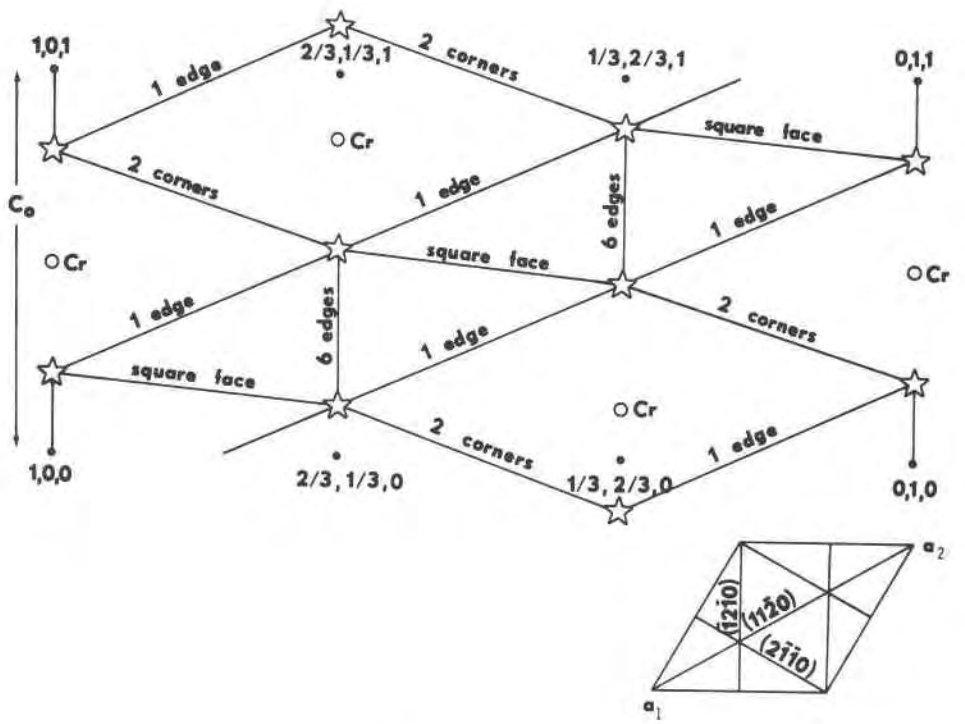

FIG. 2. A schematic view of the (11$\bar{2}$0) section of the structure of yedlinite showing the distribution of shared elements among lead-coordination pinwheel groups. All sharing elements shown as lines involve only chlorine apices and Cl-Cl edges. The star symbol represents a single three-member pinwheel. The insert at the lower right shows the locations of similar sections in the cell.

c by octahedrally coordinated chromium atoms. Three X oxygen atoms from each of two double pinwheel groups are shared with the chromium, forming the octahedral coordination.

Each lead polyhedron is tied to a symmetry-center-related polyhedron of an adjacent $\bar{3}$ axis by sharing an approximately square face composed of four chlorine atoms (lightly shaded, Fig. 1). This face sharing, coupled with additional sharing of edges and apices, serves to unite adjacent stacks to form a three dimensional bonding framework as depicted in a $(11\bar{2}0)$ section in Figure 2. This sharing scheme is repeated in all $\{11\bar{2}0\}$ planes. A projection and stereo view of the structure is shown in Figure 3.

The hydrogen atoms associated with Y oxygen atoms on the $\bar{3}$ axes are probably disordered. The single proton of (O,OH) would likely lie on the $\bar{3}$ axis and would be disordered equally between the oxygens. The large standard deviation suggests that disorder produces different positions for the oxygens of any centrosymmetric pair. The distance between the centrosymmetric Y oxygens is 2.12(.32) Å. A change of 1.5σ would give a realistic hydrogen bond distance of 2.60 Å. It is possible that something exotic is happening here, but our data is not sufficient to support further speculation. Hydrogen bonds from X-site oxygens are probably directed toward chlorines.

The prismatic cleavage, $\{11\bar{2}0\}$, of yedlinite is elegantly shown in the crystal structure. These are the only *planar* surfaces parallel to c that do not disrupt the relatively strong Cr-O or Pb-O bonds. In

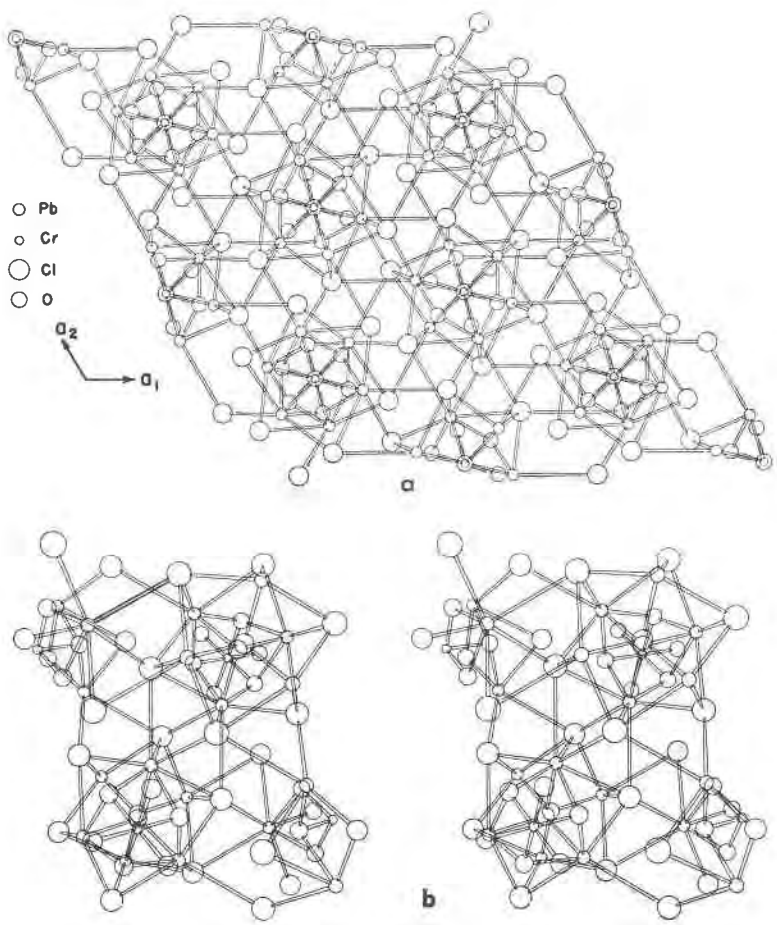

FIG. 3. The crystal structure of yedlinite viewed down the c axis by ORTEP (Johnson, 1965). **a.** In projection showing more than a full unit cell. **b.** In stereo with the $\bar{3}$ axes at 2/3, 1/3, z and 1/3, 2/3, z occupying the SW and NE quadrants, respectively. The a_1 axis is down and the a_2 axis is to the right and 30° up. Atom sizes are relatively the same as in Figure 3a.

addition to $\{11\bar{2}0\}$, many potential cleavage directions exist parallel to c in which Cr-O and Pb-O bonds would not be broken if an undulating cleavage surface was allowed. All directions parallel to c must cut across at least two of the three interstack bonding directions shown in Figure 2 and must thus break Pb-Cl bonds (a square face, a 2 corner, and two 1 edge lines of Figure 2 for each such direction cut). The lowest density of interstack bonding directions to be broken occurs in the $(11\bar{2}0)$ direction. The only directions which are not parallel to the c axis in which cleavage would not disrupt Cr-O or Pb-O bonds are the $\{10\bar{1}1\}$ directions. Such a cleavage would break many Pb-Cl bonds and the hydrogen bonds between Y-site oxygen atoms and is not observed (this would be a lower left to upper right break in Figure 2, transecting the square face and 6 edge lines).

Acknowledgments

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