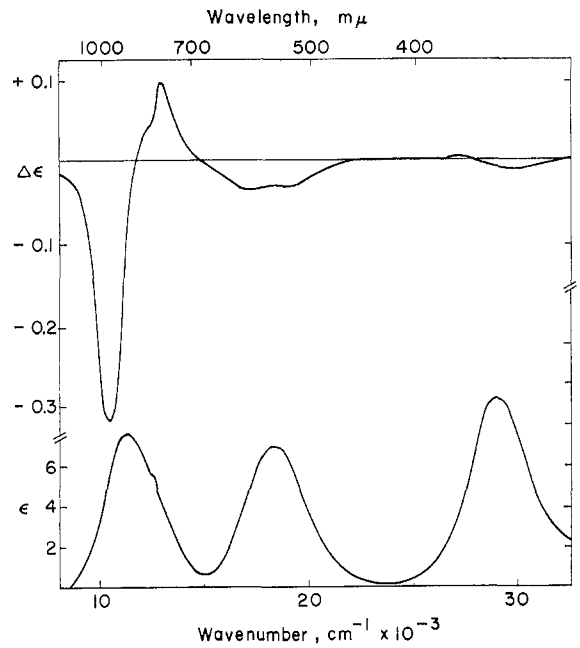

Figure 1.—CD and absorption spectra of $[Ni(l\text{-chn})_3]Cl_2 \cdot 3H_2O$ in anhydrous methanol.

metal ion is considered in greater detail. $Ni(l\text{-chn})_3{}^{2+}$ can exist in either the Δ or Λ configuration.[12] With a knowledge of the absolute configuration of the ligand these configurations are known to have the *lel* and *ob* conformations, respectively.[13] The former is thermodynamically more stable. Thus, it can be assumed that the CD spectrum is predominantly that of the Δ, *lel* diastereoisomer. The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition has first a large, negative and then a smaller, positive CD component. The very same characteristic is found for the magnetically allowed, $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of $(-)_{T_{1g}}$-$[Co(l\text{-chn})_3]Cl_3$, which is known to have the Δ, *lel* configuration.[14] Thus, an example of the correlation of circular dichroism and absolute configuration has been found which spans d^6 and d^8 metal ions. This implies that the criterion of McCaffery, Mason, and Ballard[6] may extend beyond d^3 and d^6 cases. Indeed, a theoretical basis for this proposal is contained in the expressions of Liehr for the rotational strengths of trigonal complexes.[4]

Assignments of the various CD band components can be made by reference to the D_3 point group. The negative and positive components of the first band are assigned $^3A_2 \rightarrow {}^3E$ and $^3A_1$, respectively, in keeping with the pattern established by d^3 and d^6 tris-1,2-diamine complexes.[6b] The spike appearing on the positive component is attributed to the singlet state, ^1E, which is strongly mixed with the near-lying triplet states. The second and third absorption bands each have ^3E and $^3A_2$ components in D_3. Since transitions to $^3A_2$ are electrically and magnetically forbidden, each of the bands is expected to have only a single CD component, ^3E. In both cases, however, two CD bands are evident indicating a removal of the degeneracy of the ^3E state. This is possibly the result of spin–orbit coupling or a loss of D_3 symmetry through ion pairing.

Acknowledgment.—The author is indebted to the late Professor T. S. Piper, under whose direction this research was begun.

---

[12] T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

[13] F. Woldbye, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 197 (1963).

[14] T. S. Piper and A. G. Karipides, *J. Am. Chem. Soc.*, **86**, 5039 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
POLYTECHNIC INSTITUTE OF BROOKLYN,
BROOKLYN, NEW YORK 11201

New Analogs of Spodiosite, Ca_2VO_4Cl and Ca_2AsO_4Cl

BY E. BANKS, M. GREENBLATT, AND R. W. SCHWARTZ

Received July 27, 1967

Recently the crystal structures of Ca_2PO_4Cl and Ca_2CrO_4Cl, analogs of the mineral spodiosite, Ca_2PO_4F, have been determined.[1] These crystals are orthorhombic, space group Pbcm, with four molecules per unit cell. The structure contains distinct oxygen tetrahedra, $MO_4{}^{3-}$, which appear to be held together by the calcium ions. The crystal structures indicate that these tetrahedra are distorted, this distortion being greater for the chromate(V) than for the phosphate. This has been attributed to an electronic ordering of the single d electron in the e orbitals of the $CrO_4{}^{3-}$ complex.[2]

It was also noted that the infrared vibrational spectrum of these two species showed splitting of the band associated with the asymmetric stretch.[2] This splitting is greater for the chromate(V) and is attributed to the greater distortion of the $CrO_4{}^{3-}$ tetrahedra.

This paper reports the results of an attempt to prepare new phases with the spodiosite structure and to determine if the extra distortion in the $CrO_4{}^{3-}$ ion is indeed attributable to electronic ordering. Attempts were made to prepare such compounds using V, As, Sb, Mo, and W as possible central atoms.

Experimental Section

All samples were prepared from a $CaCl_2$ flux. The metallic oxide, $CaCO_3$, and the flux were mixed in a 30-ml Pt crucible and in mole ratios of 1:3:12. The crucibles were covered and placed in a furnace. The samples were soaked for 16 hr at 900° under an oxygen atmosphere and then cooled to about 200° at a rate of 14.5°/hr.

After cooling to room temperature the crucibles and product were boiled in distilled water. The product was washed on a Büchner funnel until no sign of Cl^- could be detected with silver nitrate solution. This indicated that all of the flux had been washed away. The product was obtained in both crystal and powder form. Separation of the powder was accomplished by placing the product in a beaker with distilled water and after

---

[1] E. Banks, M. Greenblatt, and B. Post, *Acta Cryst.*, **23**, 166 (1967).

[2] E. Banks, M. Greenblatt, and B. R. McGarvey, *J. Chem. Phys.*, **47**, 3772 (1967).

3-5 min of agitation quickly decanting the liquid. This took almost all of the powder off as a suspension in the water.

X-Ray diffraction powder patterns were run on a Norelco diffractometer, using filtered copper radiation. Infrared spectra were recorded on a Perkin-Elmer Model No. 521 between 2.5 and 40 μ, using KBr pellets. Densities of single-crystal specimens were determined by flotation in standard liquids (Cargille).

Results

The only samples to show a diffraction pattern and infrared spectrum similar to the phosphate and chromate(V) chlorospodiosites were the vanadate, Ca_2VO_4Cl, and the arsenate, Ca_2AsO_4Cl.

The diffraction patterns for these two phases are given in Table I. These patterns are from the crystal part of the product. For the vanadate this is exactly the same as the powder part of the product, while for the arsenate there are some slight differences between the two patterns. These patterns resemble quite closely those reported by Banks, Greenblatt, and Post[1] and by Banks and Jaunarajs.[3]

Table I

Powder Patterns for Ca_2VO_4Cl and Ca_2AsO_4Cl

Ca_2VO_4Cl				Ca_2AsO_4Cl		
I	$d_{obs.}$	$d_{cal.}$	hkl	I	$d_{obs.}$	$d_{cal.}$
10	6.31	6.31	100	25	6.33	6.33
45	5.52	5.52	002	85	5.53	5.52
10	4.72	4.73	110	15	4.72	4.72
80	4.35	4.35	111	30	4.34	4.34
			102	10	4.16	4.16
			112	15	3.59	3.59
65	3.57	3.57	020	65	3.55	3.55
10	3.16	3.16	200			
65	2.998	2.999	022	100	2.986	2.988
75	2.884	2.887	210	50	2.888	2.888
25	2.791	2.793	211	10	2.796	2.794
100	2.763	2.763	004	40	2.761	2.762
25	2.740	2.740	202	15	2.743	2.743
55	2.707	2.709	122	30	2.701	2.701
80	2.557	2.558	212	40	2.560	2.559
5	2.529	2.531	104			
			114	5	2.384	2.385
35	2.364	2.364	220	10	2.361	2.361
10	2.312	2.312	221	5	2.310	2.309
20	2.272	2.272	213	5	2.273	2.273
5	2.227	2.227	130			
5	2.184	2.185	024	5	2.179	2.180
			222	5	2.173	2.172
25	2.066	2.065	124	5	2.062	2.061
20	2.002	2.002	115	5	2.002	2.002
55	1.996	1.996	214	15	1.996	1.996
20	1.966	1.966	302	5	1.969	1.969
20	1.900	1.900	230	5	1.895	1.895
10	1.873	1.873	231			
45	1.797	1.797	232	15	1.792	1.792
20	1.785	1.785	040	15	1.776	1.776
10	1.674	1.674	304	5	1.675	1.675
5	1.639	1.640	142			
			026	5	1.635	1.635
			126	5	1.583	1.583
			400	5	1.581	1.581
10	1.566	1.566	234	10	1.562	1.562
5	1.554	1.554	240			
			216	10	1.552	1.553
5	1.517	1.517	402			
			044	5	1.484	1.484
20	1.396	1.396	422	15	1.397	1.397
			008	10	1.381	1.381

The lattice constants for these two phases have been determined from the X-ray powder data. They are: for the vanadate, $a = 6.311$ Å, $b = 7.140$ Å, $c = 11.052$ Å; and for the arsenate, $a = 6.324$ Å, $b = 7.104$ Å, $c = 11.048$ Å. The estimated error for all of these dimensions is ± 0.005 Å.

The quantity of crystals obtained in both cases where spodiosite patterns were obtained was insufficient for conventional chemical analysis. Small samples were sent for microanalysis by a commercial firm, but the results were neither internally consistent, nor could they be fitted to any plausible stoichiometry. The assignment of stoichiometric compositions is based on the agreement of measured and calculated densities and on the correspondence of the X-ray and infrared data to those of the previously studied chlorospodiosites. The densities found for Ca_2VO_4Cl and Ca_2AsO_4Cl were 3.06 and 3.42 g/cm^3, which agree reasonably with the values of 3.07 and 3.41 g/cm^3, based on the X-ray data and the assumed stoichiometry.

Figure 1a shows the prominent part of the infrared spectrum of the vanadate. This is once again identical with the spectrum of the powder phase. Figure 1b is the infrared spectrum of the crystal part of the arsenate while Figure 1c is that of the powder part of that

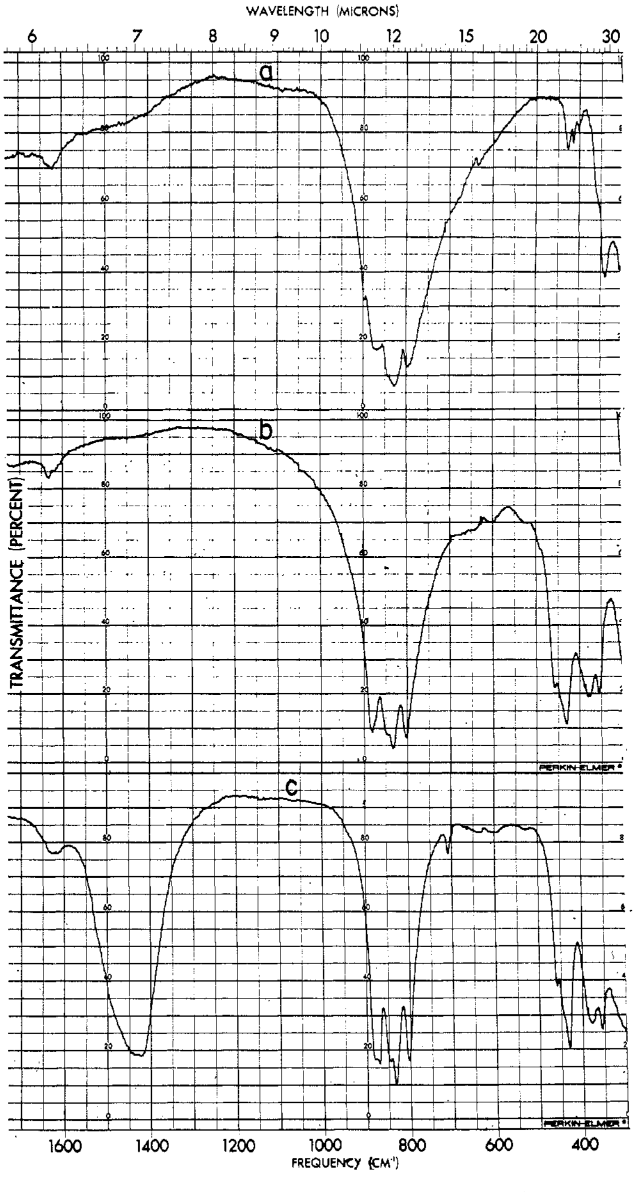

Figure 1.—Infrared spectrum of chlorospodiosites: (a) Ca_2VO_4Cl; (b) Ca_2AsO_4Cl (crystals); (c) Ca_2AsO_4Cl (powder product).

---

[3] E. Banks and K. Jaunarajs, *Inorg. Chem.*, **4**, 78 (1965).

product. The intense absorption around 7 μ has not been explained but may be due to an amorphous phase, because the diffraction patterns of the crystal and powder parts of this product show only a slight difference. There is no sign of a band in this region from the crystalline Ca_2AsO_4Cl or of an analogous band in Ca_2VO_4Cl.

The infrared spectra of these two phases clearly show that the band around 12 μ is split much more for the vanadate than for the arsenate, although the spectrum of the vanadate is not as clearly resolved. A comparison of the vanadate with the phosphate and chromate shows its splitting to be between that of the other two while the arsenate has the smallest splitting of the four.

Conclusion

It is concluded from the X-ray, infrared, and density data that the vanadate and the arsenate have the formulas attributed to them and that each has the spodiosite structure. The probable reactions of formation for these two species are

$$3CaCO_3 + V_2O_5 + CaCl_2 \longrightarrow 2Ca_2VO_4Cl + 3CO_2 \quad (1)$$

$$3CaCO_3 + As_2O_3 + CaCl_2 \xrightarrow{O_2} 2Ca_2AsO_4Cl + 3CO_2 \quad (2)$$

Since the amount of splitting of the asymmetric stretch bands in the infrared spectrum is known to increase with increasing distortion of the oxygen tetrahedron and the amount of splitting is observed to be in the order AsO_4^{3-}, PO_4^{3-}, VO_4^{3-}, CrO_4^{3-}, with the CrO_4^{3-} splitting being over 50% more than that of the others, it appears that the extra distortion in the CrO_4^{3-} ion is attributable to electronic effects, as discussed by Banks, Greenblatt, and McGarvey.[2] They proposed that the ordering of the single d electron into the d_{z^2} orbital, as shown by esr data, is responsible for the extra distortion above that introduced by the packing of the tetrahedra in the spodiosite structure. The differences in distortion of the other three species appear to be small and cannot be correlated with any obvious differences in the properties of the central atoms.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

The Reaction between Chromate and Thiosulfate. I. The Chromatothiosulfate Intermediate

BY I. BALDEA AND G. NIAC[1]

Received August 14, 1967

Oxidations by chromate ion often occur through formation in the first step of intermediates arising by elimination of water molecules. Such intermediates were proposed for the oxidation of alcohols by Leo and Westheimer[2a] and for the oxidation of arsenite by Mason and Kowalak.[2b] Similar intermediates could reasonably be expected in the chromate oxidation of thiosulfate, but until now no data were available on the kinetics of this reaction and the nature of the intermediates. It was the goal of the present work to search for evidence of the formation of an intermediate using spectrophotometric means.

Since the redox reaction under consideration has a half-time of 10–50 sec under the acidic conditions used, kinetic records of the absorbance were made during the reaction, and values extrapolated to zero time were used to determine the molar absorptivity of the intermediate and the equilibrium constant for its formation. A flow device was used to record the absorption spectrum of the intermediate at steady state.

Experimental Section

Chemicals.—Merck Analytical grade chemicals were used without further purification. The $NaClO_4$ was prepared by neutralization of $HClO_4$ with NaOH of known concentration. The equivalence point was established by means of a glass-electrode pH meter. The solutions were made using twice distilled water (over $KMnO_4$). Air was eliminated by bubbling natural methane gas from which traces of O_2 were removed by an alkaline pyrogallol solution and mercaptans were removed by adsorption on active carbon.

Kinetic Runs.—These were performed by a syringe technique, introducing 1 ml of the Cr(VI) solution into a photometer cell of 10-mm path length containing 4 ml of the thiosulfate solution. Both solutions were prepared from stock solutions of $Na_2S_2O_3$, $K_2Cr_2O_7$, $HClO_4$, and $NaClO_4$. The needed amount of $HClO_4$ was added to the Cr(VI) solution, while the $NaClO_4$ was added to the thiosulfate solution.

The mixing time was found to be less than 0.4 sec, determined by mixing under the same conditions a methylene blue solution with water and recording the process photometrically using a photomultiplier and an oscilloscope.

The reaction itself was followed by means of a spectrophotometric device composed of a VSU 1 spectrophotometer (manufactured by Zeiss-Jena), provided with a hydrogen lamp, a photocell, and a Wulff string electrometer, the image of which was projected on the inlet slit of a photographic recorder. This device was able to record a transmitted light intensity *vs.* time curve. The spectral slit width was 1 mμ. The photometric cell was surrounded by a temperature jacket with tube connections to a thermostat. The photographic records were enlarged and then used to calculate the absorbance at zero time, *i.e.*, at the time of mixing.

Continuous-Flow Technique.—This technique was used to record the absorption spectra at reaction times close to zero. The records were made with a Beckman Model DB spectrophotometer, adapting to the 1-cm cell a mixing chamber, shown in Figure 1, following the design of Dixon's cell used for electron spin resonance studies.[3] The two reagent solutions flowed from two 10-l. flasks through the mixing chamber into the photometer cell. A thermometer placed in the exit tube of the photometer cell served to indicate the reaction temperature. The time elapsed between the mixing of solutions and their crossing the light beam was about 0.5 sec.

The over-all flow velocity was determined for the flow of 200 ml of solution, and the mixing ratio for the two solutions was determined by titration of the excess of one of the reactants after the reaction was terminated. The flow velocity was between 2

---

(1) Visiting Scholar at Stanford University, 1966–1967, from the University of Cluj, Cluj, Rumania, during which time this paper was prepared.

(2) (a) A. Leo and F. H. Westheimer, *J. Am. Chem. Soc.*, **74**, 4383 (1952); (b) I. G. Mason and A. D. Kowalak, *Inorg. Chem.*, **3**, 1248 (1964).

(3) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963).