(14) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(15) R. F. Stewart, J. T. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(16) "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, p 202.
(17) G. J. Visser, G. J. Heeres, J. Walters, and A. Vos, *Acta Crystallogr., Sect. B*, **24**, 467 (1968).
(18) Supplementary material.
(19) D. W. J. Cruickshank et al., "Computing Methods and the Phase Problem in X-Ray Crystal Analysis", R. Pepinsky et al., Ed., Pergamon Press, Oxford, 1961.
(20) E. M. Bradley, J. Chatt, R. L. Richards, and G. A. Sim, *J. Chem. Soc. D*, 1322 (1969).
(21) C. Panattoni, R. Bombiere, E. Forsellini, B. Crocioni, and V. Belluco, *J. Chem. Soc. D*, 187 (1969).
(22) B. M. Craver, and D. Hall, *Acta Crystallogr.*, **21**, 177 (1966).
(23) D. Moros, J. Dehand, and R. Weiss, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **276**, 1471 (1968).
(24) V. G. Albano, P. L. Bellon, and M. Sansori, *Inorg. Chem.*, **8**, 298 (1969), and references contained therein.
(25) W. Eventoff, Ph.D. Thesis, University of Michigan, 1972.
(26) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Substitution", Wiley, New York, N.Y., 1967, pp 351–375.
(27) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination", Macmillan, New York, N.Y., 1968, pp 421–425.
(28) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1967, pp 45, 115.
(29) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 791 (1962).
(30) J. P. Beale and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **27**, 73 (1971).
(31) "International Tables for X-Ray Crystallography", Vol. II, Kynoch Press, Birmingham, England, 1962, p 276.
(32) W. R. Mason, III, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).
(33) J. Chatt, G. A. Gamelin, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).
(34) J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, **92**, 7306 (1970).
(35) G. Dolcetti, A. Peloso, and L. Sindarelli, *Gazz. Chim. Ital.*, **96**, 1948 (1966).
(36) A. R. Katritzky and A. P. Ambler, "Physical Methods in Heterocyclic Chemistry", Vol. 2, A. R. Katritzky, Ed., Academic Press, New York, N.Y., 1963, pp 205–208.
(37) O. H. S. Greer, W. Kynaston, and H. M. Paisley, *Spectrochim. Acta*, **19**, 549 (1963).

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Crystal Chemistry of Struvite Analogs of the Type $MgMPO_4 \cdot 6H_2O$ ($M^+ = K^+, Rb^+, Cs^+, Tl^+, NH_4^+$)[1]

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The crystallographic properties and the infrared absorption spectra of the struvite analogs of the type $MgMPO_4 \cdot 6H_2O$ where $M^+ = K^+$, Rb^+, Cs^+, Tl^+, or NH_4^+ are reported. The relative stabilities of the struvite analogs are discussed in terms of the radii of the univalent ions.

I. Introduction

The mineral struvite ($MgNH_4PO_4 \cdot 6H_2O$) is often found associated with living or decomposing organisms. It has been described in ref 3 as being found in dung, putrescent matter, canned foods, and bladder or kidney concretions. The crystal structure was solved with a crystal obtained from a tin of salmon. This structure was based on the earlier work of Bland and Basinski[4] and Whitaker and Jeffery.[5,6] The analogous compound $MgKPO_4 \cdot 6H_2O$ was reported as forming an isomorphous series with struvite by Lehr et al.[7] The infrared spectra, X-ray diffraction patterns, and optical and crystallographic properties of struvite and the potassium analog were also reported. Struvite has been compared to the related compound $CaKAsO_4 \cdot 8H_2O$,[8] and their biological importance as possible precursors of nuclei of crystallization has been noted. The apparently related materials $MgCsPO_4 \cdot 6H_2O$ and $MgCsAsO_4 \cdot 6H_2O$ have also been reported by Ferrari et al.[9,10] It is the purpose of this report to study the substitution of alkali metals and "pseudoalkali" cations in the struvite crystal structure.

II. Experimental Section

All crystals were grown by means of the gel diffusion technique. The growth of struvite by the gel diffusion method has been reported by Banks et al.[11,12] An aqueous solution of 0.05 *M* $MgSO_4$ and 0.04–0.02 *M* M_2EDTA (EDTA = ethylenediaminetetraacetate) was adjusted to pH 10 with MOH. Eastman Kodak "ultrapure" calfskin gelatin was dissolved in the resulting solution (55 g/l.) and allowed to set. Before setting, several drops of formaldehyde were added to strengthen the gel and to prevent growth of molds. Generally 100 ml of gel was set in a 250-ml electrolytic beaker. When the gel had set an equivalent amount of a solution of 0.05 *M* $M_2HPO_4 \cdot xH_2O$ which had been adjusted to pH 10.0 with MOH was carefully poured over the gel. The beaker was covered and the crystal growth proceeded at the gel–liquid interface and into the gel. Experiments were complete within several weeks and the crystals were harvested. Photographs of the resulting crystals may be seen in Figure 1.

All reagents used were Baker Analyzed reagents except the Eastman Kodak calfskin gelatin. Rubidium and cesium phosphates were prepared by neutralizing H_3PO_4 with an equivalent amount of RbOH or CsOH in situ. Rubidium, ammonium, potassium, and cesium salts of EDTA were prepared by neutralizing H_2EDTA with an equivalent amount of RbOH or CsOH also in situ. In the case of the thallium salt $TlNO_3$ was used as a source of thallium and Na_2EDTA and NaOH were used. The presence of sodium did not interfere with the growth of $MgTlPO_4 \cdot 6H_2O$ or any of the other struvite analogs and Na_2EDTA can replace the M_2EDTA.

X-Ray powder patterns were taken on a Norelco powder diffractometer with monochromated Cu Kα radiation with KCl as an internal standard.

Infrared spectra were taken on a Perkin-Elmer Model 521 spectrometer with the sample in a KBr disk.

Crystal densities were measured either by pycnometric means or by the sink–float method.[13]

Chemical analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

Crystal size and perfection can be optimized by varying the conditions described above. Table I shows the best conditions tried for each material and the results obtained.

III. Crystallographic Properties

Crystals of struvite occurred in both wedge-shaped prisms and needles. Twins on (001) such as described by Palache et al.[3] are frequently seen. Both $MgKPO_4 \cdot 6H_2O$ and $MgRbPO_4 \cdot 6H_2O$ were seen only in needle form. $MgTlPO_4 \cdot 6H_2O$ grew in wedge-shaped, distinctly struvite-like crystals and in other shapes. Crystals of $MgCsPO_4 \cdot 6H_2O$ were capped hexagonal prisms or trigonal pyramids as described by Ferrari et al.[9,10] All crystals were stable for short periods when taken from their mother liquor except $MgRbPO_4 \cdot 6H_2O$ which clouded easily. Struvite crystals may be stored in a capped bottle indefinitely but all other crystals showed a tendency to hydrolyze to a greater or lesser extent over long periods of time. However, the NH_4^+, Tl^+, and Cs^+ crystals showed a greater degree of stability than the K^+ or Rb^+ crystals. Table II

Table I

Compd	Gel soln	Top soln	Remarks
$MgKPO_4 \cdot 6H_2O$	0.05 *M* $MgSO_4$ 0.04 *M* K_2EDTA pH 10 KOH	0.05 *M* K_2HPO_4 pH 10 KOH	Needles up to 1 cm
$MgRbPO_4 \cdot 6H_2O$	0.010 *M* $MgSO_4$ 0.005 *M* Rb_2EDTA pH 10 RbOH	0.010 *M* Rb_2HPO_4 pH 10 RbOH	Needles up to 1 cm
$MgCsPO_4 \cdot 6H_2O$	0.05 *M* $MgSO_4$ 0.02 *M* Cs_2EDTA pH 10 CsOH	0.05 *M* Cs_2HPO_4 pH 10 CsOH	Hexagonal pyramids or pyramidal prisms up to several millimeters
$MgNH_4PO_4 \cdot 6H_2O$	0.05 *M* $MgSO_4$ 0.04 *M* $(NH_4)_2EDTA$ pH 10 NH_4OH	0.05 *M* $(NH_4)_2HPO_4$ pH 10 NH_4OH	Needles up to 3 cm or prisms up to 5 mm
$MgTlPO_4 \cdot 6H_2O$	0.05 *M* $MgSO_4$ 0.04 *M* Na_2EDTA pH 10 NaOH	0.05 *M* Na_2HPO_4 0.05 *M* $TlNO_3$ pH 10 NaOH	Wedge-shaped prism up to 5 mm

Table II. Crystallographic Properties

Compd	System	*a*, Å	*b*, Å	*c*, Å	*Z*	Ionic radius of M^+,[a] Å	d_x, g ml^{-1}	d_m, g ml^{-1}	Space group
$MgKPO_4 \cdot 6H_2O$	Orthorhombic	6.87[b]	11.09[b]	6.16[b]	2	1.33	1.88	1.91[b]	$Pm2_1n$
$MgTlPO_4 \cdot 6H_2O$	Orthorhombic	6.861	11.35	6.135	2	1.44	3.00	2.99	$Pm2_1n$
$Mg(NH_4)PO_4 \cdot 6H_2O$	Orthorhombic	6.95 (6.945)[c]	11.21 (11.21)[c]	6.14 (6.14)[c]	2	1.48	1.71		$Pm2_1n$
$MgRbPO_4 \cdot 6H_2O$	Orthorhombic (triclinic?)	6.852	11.27	6.177	2	1.48	2.18	2.15	$Pm2_1n$?
$MgCsPO_4 \cdot 6H_2O$	Hexagonal	6.899 (6.939)[d]		11.99 (11.99)[d]	2	1.69	2.40	2.42 (2.43)[d]	$P6_3mc$
	Cubic	10.02			4		2.38		$F43m$

[a] A. F. Wells, "Structural Inorganic Chemistry", 3rd ed, Oxford University Press, London 1967, p 71. [b] JCPDS powder diffraction file card 20-685. [c] JCPDS powder diffraction file card 15-762. [d] References 9 and 10.

Table III. Powder Diffraction Data for $MgTlPO_4 \cdot 6H_2O$[a]

hkl	d_o	d_c	I/I_0	*hkl*	d_o	d_c	I/I_0
001	6.16	6.14	10	122	2.510	2.511	10
110	5.88	5.87	100	141	2.409	2.411	5
020	5.70	5.68	10	032	2.380	2.383	5
011	5.42	5.40	60	231	2.348	2.348	5
101	4.58	4.57	50	212	2.239	2.241	10
111	4.24	4.24	55	240	2.181	2.187	3
021	4.17	4.17	60	150	2.151	2.155	3
121	3.56	3.56	65	051	2.128	2.129	3
200	3.43	3.43	10	003	2.045	2.045	3
130	3.31	3.31	50	151	2.031	2.033	5
031	3.22	3.22	20	321	2.004	2.005	5
012	2.964	2.961	30	232	1.954	1.957	10
131	2.928	2.915	10	023	1.925	1.924	5
211	2.893	2.895	25	060	1.891	1.892	3
040	2.838	2.838	10	331	1.860	1.865	3
102	2.801	2.800	10	160	1.824	1.824	3
022	2.701	2.699	20	061	1.804	1.808	3
221	2.647	2.648	10	203	1.756	1.757	3
041	2.569	2.575	3	133	1.740	1.740	3

[a] Orthorhombic: $a = 6.861$ (5), $b = 11.35$ (2), $c = 6.135$ (5) Å.

compiles the crystallographic properties of the struvite analogs as determined in this work and elsewhere.

Struvite and $MgKPO_4 \cdot 6H_2O$ gave X-ray powder patterns which agree well with JCPDS powder diffraction cards 15-762 and 20-685, respectively.

$MgTlPO_4 \cdot 6H_2O$ gave a powder pattern which can be indexed on an orthorhombic cell with $a = 6.861$, $b = 11.35$, and $c = 6.135$ Å as shown in Table III. Table IV shows the powder pattern obtained for $MgRbPO_4 \cdot 6H_2O$ which can also be indexed on an orthorhombic cell with $a = 6.852$, $b = 11.27$, and $c = 6.177$ Å. Some very weak ($I/I_0 < 5$) lines were seen which could not be indexed on this cell indicating either a second phase such as $Mg_3(PO_4)_2 \cdot 4H_2O$ or a lower symmetry for $MgRbPO_4 \cdot 6H_2O$. The latter explanation is supported by infrared evidence discussed later on.

Table IV. Powder Diffraction Data for $MgRbPO_4 \cdot 6H_2O$[a] .

hkl	d_o	d_c	I/I_0	*hkl*	d_o	d_c	I/I_0
110	5.87	5.86	15	141	2.402	2.401	10
020	5.62	5.64	5	032	2.386	2.386	10
011	5.43	5.42	30	231	2.341	2.342	10
101	4.60	4.59	40	132	2.247	2.248	10
111	4.25	4.25	100	003	2.059	2.059	5
021	4.17	4.16	80	013	2.028	2.026	10
121	3.56	3.56	25	232	1.954	1.958	15
200	3.43	3.43	35	060	1.878	1.878	5
130	3.30	3.29	40	123, 331	1.862	1.861	10
031	3.22	3.21	15	242	1.785	1.779	5
012	2.974	2.979	35	213	1.742	1.744	10
211	2.897	2.896	100	400	1.713	1.713	5
040	2.824	2.818	70	350	1.603	1.604	5
022	2.710	2.708	50	261	1.589	1.591	5
221	2.645	2.645	35	162, 170	1.565	1.563	5
041	2.569	2.563	5	024	1.489	1.489	5
122	2.517	2.519	30	153	1.484	1.484	5

[a] Orthorhombic: $a = 6.852$ (5), $b = 11.27$ (2), $c = 6.177$ (5) Å. An unindexed weak line(s) appears at $d = 4.04$ Å which can be attributed to $Mg_3(PO_4)_2 \cdot 4H_2O$.

Table V. Powder Diffraction Data for Hexagonal $MgCsPO_4 \cdot 6H_2O$[a]

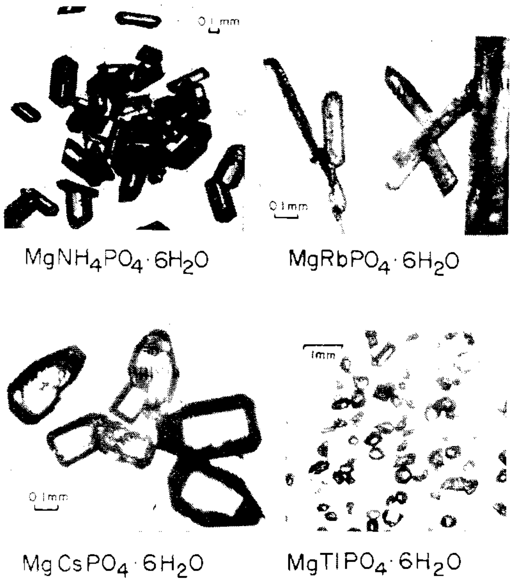
hkl	d_o	d_c	I/I_0	*hkl*	d_o	d_c	I/I_0
010	5.99	5.98	20	122	2.11	2.114	5
011	5.36	5.35	100	030	1.993	1.992	10
012	4.23	4.23	40	031	1.963	1.965	20
110	3.46	3.45	70	025	1.865	1.871	20
111	3.32	3.32	40	220	1.725	1.725	10
020	2.984	2.988	60	034	1.658	1.659	5
021	2.904	2.899	20	132	1.595	1.598	10
022	2.671	2.675	30	133	1.529	1.531	3
023	2.390	2.394	10	224	1.493	1.495	3
120	2.259	2.259	10	134	1.448	1.451	3
121	2.220	2.220	10	231	1.360	1.362	3

[a] $a = 6.899$ (5), $c = 11.99$ (2) Å.

Table VI. Powder Diffraction Data for Cubic $MgCsPO_4 \cdot 6H_2O$

hkl	d_o	d_c	I/I_0	*hkl*	d_o	d_c	I/I_0
111	5.80	5.78	30	400	2.504	2.504	100
200	5.01	5.01	100	331	2.305	2.298	10
220	3.55	3.54	35	442	2.046	2.045	5
300	3.26	3.34	10	511, 333	1.929	1.928	10
311	3.03	3.02	40	440	1.776	1.771	5

[a] a = 10.02 (2) Å.



$MgNH_4PO_4 \cdot 6H_2O$ $MgRbPO_4 \cdot 6H_2O$

$MgCsPO_4 \cdot 6H_2O$ $MgTlPO_4 \cdot 6H_2O$

Figure 1. Crystals of struvite $MgNH_4PO_4 \cdot 6H_2O$ and its Rb, Cs, and Tl analogs.

Table VII. Chemical Analyses

	$MgKPO_4 \cdot 6H_2O$		$MgRbPO_4 \cdot 6H_2O$		$MgTlPO_4 \cdot 6H_2O$		$MgTl_{0.35}(NH_4)_{0.65}PO_4 \cdot 6H_2O$	
	Theor	Exptl	Theor	Exptl	Theor	Exptl	Theor	Exptl
% Mg	9.13	9.32	7.78	7.69	5.65	5.35	7.74	6.92
% M	14.68	14.87	27.33	27.14	47.22	42.75	23.03	21.75
% P	11.63	11.74	9.91	9.79	7.18	8.63	11.29	9.51
% H_2O	40.54	39.35	34.53	33.90	25.00	24.95	40.65	37.92

Table VIII. Infrared Spectra of Struvite $MgNH_4PO_4 \cdot 6H_2O$

Band, cm^{-1}	Intens	Assignment
3700–2500	Strong, broad	Water ν_1–ν_3 sym-antisym str, NH_4^+ ν_1–ν_3 sym-antisym str
3500	Peak on 3700–2500 cm^{-1}, broad	
3250	Peak on 3700–2500 cm^{-1}, broad	
2900	Peak on 3700–2500 cm^{-1}, broad	
2500–2200	Medium, broad	Water-phosphate H bonding
1800–1500	Weak, broad	Water ν_2(H–O–H) def + $\nu_2(NH_4^+)$
1470	Weak, sharp	NH_4^+ ν_4 asym bending split by "restrictive rotation"
1430	Medium, sharp	
1390	Shoulder	
1010	Very strong, sharp	$\nu_3(PO_4^{3-})$ antisym str
880	Weak, broad	Ammonium-water H-bonding?
750	Weak, sharp	Water-water H bonding
570	Strong, sharp	$\nu_4(PO_4^{3-})$ P–O bend
450	Weak	$\nu_2(PO_4^{3-})$

Table V lists the powder pattern for $MgCsPO_4 \cdot 6H_2O$ which can be indexed on a hexagonal cell with a = 6.899 and c = 11.99 Å. The a axis is somewhat smaller than that reported by Ferrari et al.[9,10] The first product of the $MgCsPO_4 \cdot 6H_2O$ crystal growth experiments yielded a powder pattern composed of the lines reported in Table V plus the lines reported in Table VI. When the experiment was performed at 4° only the lines appearing in Table V were seen. Subtracting the lines for the hexagonal $MgCsPO_4 \cdot 6H_2O$ resulted in the powder diffraction pattern appearing in Table VI. This pattern could be indexed on a cubic cell with a = 10.02 (2) Å. The cubic $MgCsPO_4 \cdot 6H_2O$ is the analog of $MgCsAsO_4 \cdot 6H_2O$ with a = 10.18 (1) Å which was reported by Ferrari et al.[9,10] They also discussed the structure of this cubic material which has the AsO_4^{3-} group located on the body diagonal of the cube. The conditions for obtaining the pure cubic form have not been established but it appears to be a higher temperature form.

The structural relation between struvite-like materials has been discussed by Dickens et al.[8] The structures of the orthorhombic, hexagonal, and cubic materials discussed above are closely related. The magnesium atom is surrounded by an octahedron of water molecules. The difference in the lattice types of these materials is governed by the size of the alkali or "pseudoalkali" ion. For K, Tl, and NH_4 the orthorhombic struvite structure is the most stable. For cesium the higher symmetry hexagonal and cubic structures are preferred. The lower stability and more complex powder pattern of the Rb analog suggest that it has a transitional structure of perhaps lower symmetry. The possibility of mixed-alkali struvite analogs seems likely and this has been confirmed for the ammonium ion, as discussed below.

Polarizing microscope studies confirmed the crystallographic assignments described above. SHG (second harmonic generation) measurements with a neodymium glass laser gave positive results indicating acentric space groups for all the struvite analogs. This is in agreement with the X-ray and piezoelectric results of Whitaker and Jeffery,[5,6] who reported an acentric space group for struvite.

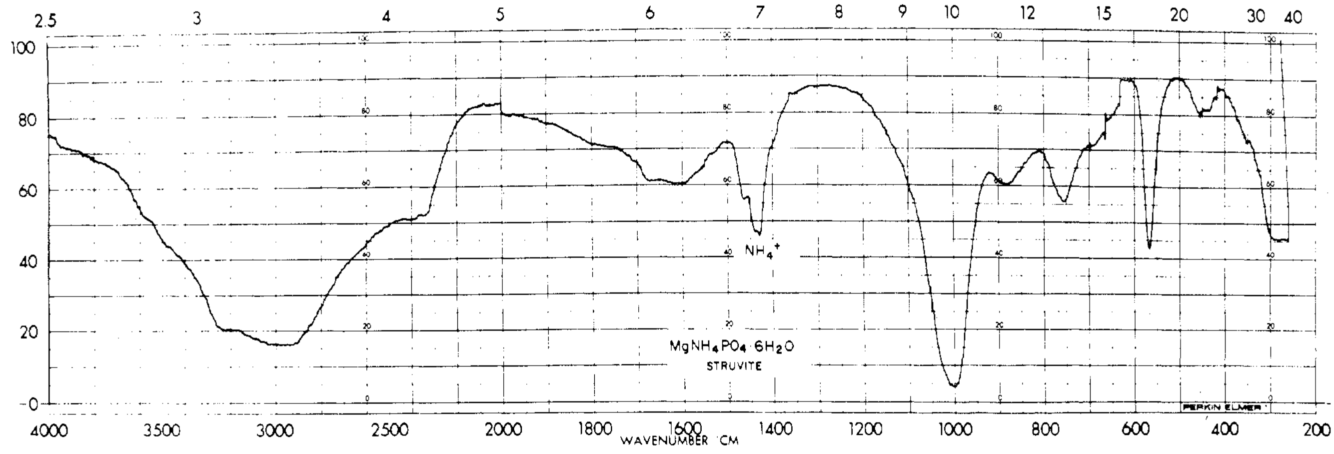


Figure 2. Infrared spectrum of $MgNH_4PO_4 \cdot 6H_2O$.

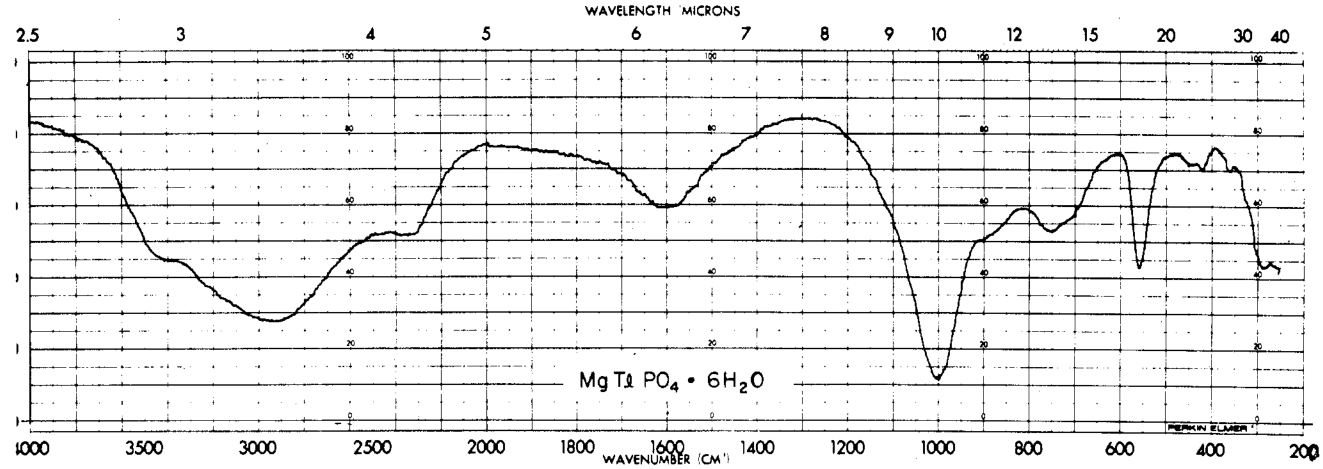


Figure 3. Infrared spectrum of $MgTlPO_4 \cdot 6H_2O$.

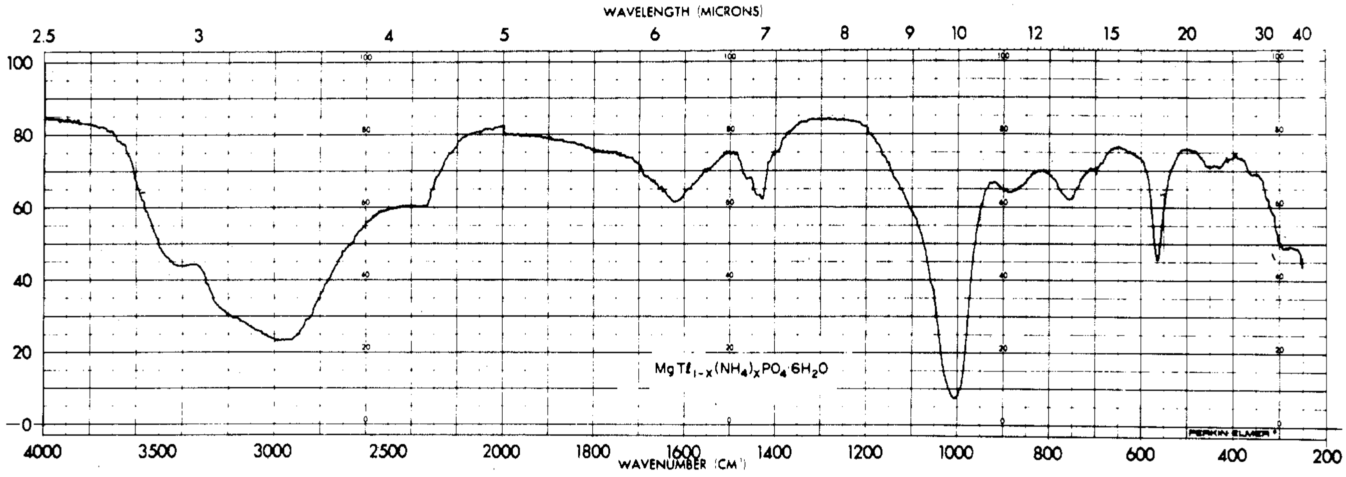


Figure 4. Infrared spectrum of $MgTl_{1-x}(NH_4)_xPO_4 \cdot 6H_2O$.

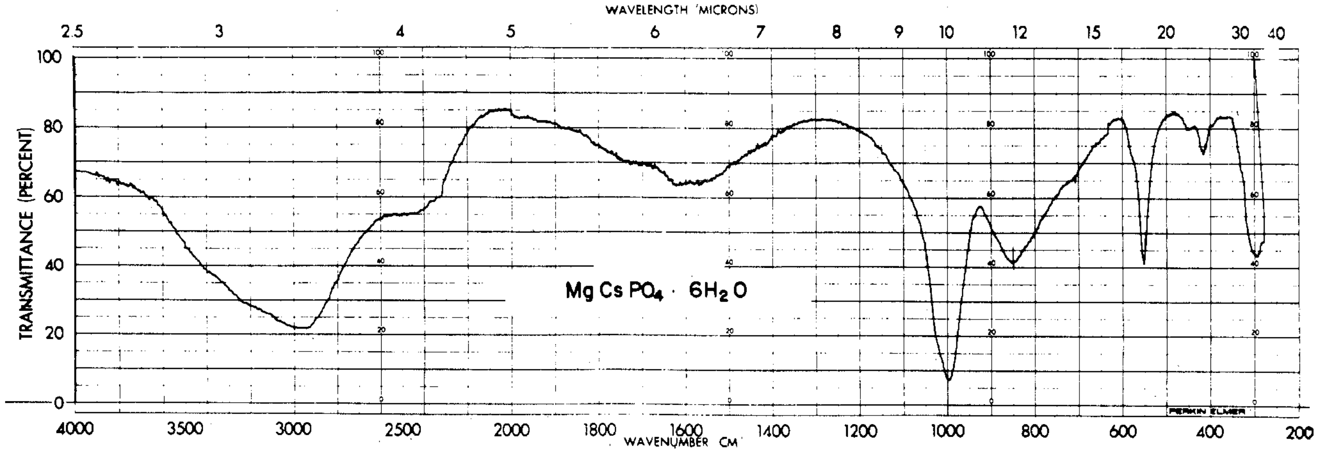


Figure 5. Infrared spectrum of $MgCsPO_4 \cdot 6H_2O$.

IV. Chemical Analyses

Chemical analyses for the K, Rb, Tl, and Tl–NH4 analogs are shown in Table VII. In some experiments the beakers containing the gels were covered with a paraffin sheet and placed in a refrigerator. The refrigerator contained ammonia in the atmosphere from other experiments containing ammonia; the ammonia would diffuse through the paraffin film and dissolve in the crystal growing solution. This resulted in mixed $MgM_{1-x}(NH_4)_xPO_4 \cdot 6H_2O$ crystals. The powder patterns of these materials showed a single phase. The infrared spectra showed the presence of the ammonium group. This substitution was observed in the cases of Rb, K, and Tl. The substitution of NH_4^+ in $MgKPO_4 \cdot 6H_2O$ was noted by Lehr et al.[7]

Although sodium was present in many of the experiments as Na_2EDTA, chemical analyses never revealed any significant sodium substitution nor was any sodium struvite analog ever seen, suggesting that the struvite structure cannot accommodate univalent ions smaller than K^+ at room temperature.

V. Infrared Data

The infrared spectra of the struvite analogs are shown in Figures 2–7. The infrared spectra of $MgNH_4PO_4 \cdot 6H_2O$ and $MgKPO_4 \cdot 6H_2O$ were previously reported by Lehr et al.[7] but no assignments were made. The assignments for struvite are shown in Table VIII and the assignments for the other struvite analogs are shown in Table IX. The spectra and assignments for the struvite analogs are very similar to those reported by

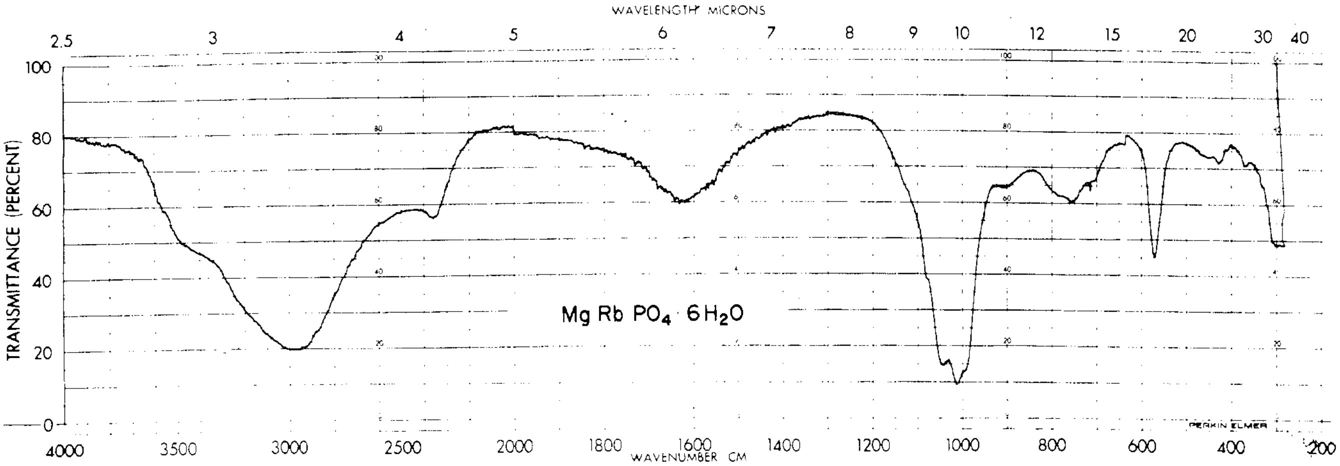


Figure 6. Infrared spectrum of $MgRbPO_4{\cdot}6H_2O$.

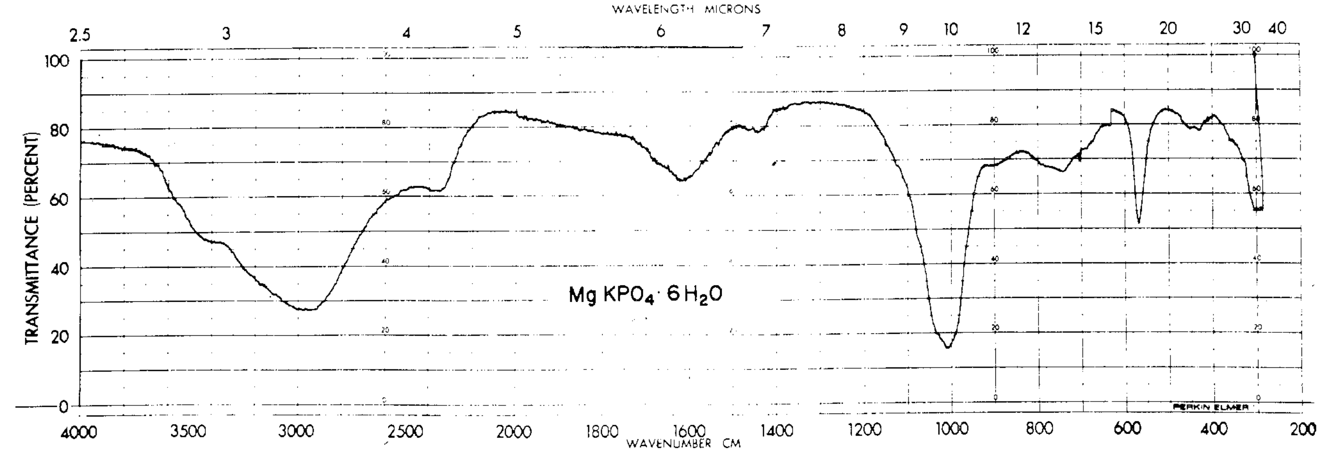


Figure 7. Infrared spectrum of $MgKPO_4{\cdot}6H_2O$.

Table IX. Infrared Spectra of the Struvite Analogs (cm^{-1})

$MgKPO_4{\cdot}6H_2O$	$MgTlPO_4{\cdot}6H_2O$	$MgRbPO_4{\cdot}6H_2O$	$MgCsPO_4{\cdot}6H_2O$	Intens	Assignment
3700-2500	3700-2500	3700-2500	3700-2500	Strong, broad	Water ν_1-ν_3 sym-antisym str
3450	3500	3500		Shoulder	
2950	2950	2950	2950	Peak of 3700-2500 cm^{-1}	
2350	2350	2350	2350	Weak	Water-phosphate hydrogen bonding
1630	1600	1630	1600	Weak, broad	Water ν_2(H-O-H) def
1070 vw[a]		1080		Shoulder	$\nu_3(PO_4^{3-})$ P-O antisym str
1040 vw		1045	1030 vw	Shoulder	
1015	1000	1015	995	Strong, sharp	
		990		Shoulder	ν_1(P-O) sym str
900	900	900		Very weak, broad	
730	750	750	850	Medium	Water-water H bonding
680	700	700		Shoulder	
			575	Shoulder	
565	565	565	550	Strong, sharp	$\nu_4(PO_4^{3-})$ P-O bend
430	440	430	415	Weak, sharp	$\nu_2(PO_4^{3-})$

[a] vw = very weak.

Banks et al.[12] for the compounds $BaNaPO_4{\cdot}9H_2O$ and $SrNaPO_4{\cdot}9H_2O$. The assignments for the NH_4^+ absorption spectra are based upon the assignments for NH_4^+ in NH_4Cl reported by Plumb et al.[14]

Plumb et al.[14] and Levy et al.[15] discussed the rotation of the NH_4^+ group in NH_4Cl. They concluded that the ammonium group was rotating about its threefold axis in a restricted manner, on the basis of the splitting of the ν_4 asymmetric bending band of the NH_4^+ group. This splitting is also observed in the infrared spectrum of struvite. This agrees with the restricted rotation of the NH_4^+ group in struvite, deduced from X-ray data by Whitaker et al.[5,6]

The splitting of the ν_3 asymmetric stretch absorption band which occurs near 1000 cm^{-1} is a quantitative measure of deviation of the PO_4^{3-} group from ideal tetrahedral symmetry. This ν_3 band is triply degenerate if the tetrahedron is perfect and the degeneracy will lift if the tetrahedron is distorted. Distortion of the PO_4^{3-} tetrahedron will also cause the infrared-inactive ν_1 symmetric stretch to appear weakly in the infrared. This distortion of the PO_4^{3-} group, if severe, may lead to a lower symmetry of the crystal lattice. $MgCsPO_4 \cdot 6H_2O$, $MgNH_4PO_4 \cdot 6H_2O$, and $MgTlPO_4 \cdot 6H_2O$ show smooth sharp ν_3 absorption bands with little or no splitting, and no ν_1 absorption band is observed. Tl^+ has an ionic radius close to that of NH_4^+ and therefore the compound would be expected to be similar to struvite. $MgCsPO_4 \cdot 6H_2O$ has a new structure of high symmetry. From this it is concluded that the Cs, Tl, and NH_4^+ analogs have regular tetrahedral PO_4^{3-} groups; this agrees with the observation of Whitaker et al.[5,6] that the tetrahedral angles of PO_4^{3-} deviate less than 1° from ideal. The alkali ions in $MgKPO_4 \cdot 6H_2O$ and $MgRbPO_4 \cdot 6H_2O$ have ionic radii which are farther from NH_4^+ and both show splitting of the ν_3 absorption band. In $MgRbPO_4 \cdot 6H_2O$ the splitting is severe and the ν_1 absorption band can be seen at 990 cm^{-1}. This indicates a lower symmetry for the Rb analog and possibly the K analog. This is consistent with the observation that these two are the least stable of the struvite analogs. Apparently K^+ and Rb^+ do not fit as well into the struvite structure as the larger ions. The Rb analog is transitional between the struvite structure and the $MgCsPO_4 \cdot 6H_2O$ structure. This raises the possibility of phase transitions in $MgRbPO_4 \cdot 6H_2O$.

In other respects the infrared spectra of the struvite analogs are remarkably similar. This might be expected as the spectra basically reflect the $(Mg(H_2O)_6PO_4)^-$ host lattice and the changes in the spectra are due to the interaction of the univalent ions with the PO_4^{3-} groups in this host lattice.

VI. Conclusions

The struvite structure shows a tendency to incorporate univalent ions ranging in size from 1.33 Å for K 1.69 Å for Cs. For K^+ (R = 1.33 Å), Tl^+ (R = 1.44 Å), NH_4^+ (R = 1.48 Å), and Rb^+ (R = 1.48 Å) the structure is orthorhombic. For the larger Cs^+ (R = 1.69 Å) ion, a hexagonal structure becomes stable. The Tl^+ analog appears to be the most stable and the NH_4^+ analog is also reasonably stable at room temperature, possibly due to hydrogen bonding. Both the K^+ and Rb^+ compounds decompose with time when removed from the mother liquor, indicating that the larger and smaller ions are somewhat strained in the orthorhombic structure. The hexagonal form of the Cs^+ analog also may transform to a cubic form at higher temperatures.

The struvite analogs offer a unique opportunity to study the effect of ionic size on a family of hydrated phosphates. The substitution of NH_4^+ into the struvite lattice containing K^+, Rb^+, and Tl^+ has been observed. Only one of these preparations was chemically analyzed; it has the approximate composition $MgTl_{1/3}(NH_4)_{2/3}PO_4 \cdot 6H_2O$. Whether or not this composition is fortuitous is not known. A study of the system $MgM_xM'_{1-x}PO_4 \cdot 6H_2O$ would yield valuable information about ordering, site preference, and the effect of ionic size on this structure. We do not know whether a reversible transition exists between hexagonal and cubic $MgCsPO_4 \cdot 6H_2O$. We do know that at 40° only the hexagonal phase was observed and at higher temperatures mixtures of hexagonal and cubic phases were observed. However, the cubic phase was not seen without the presence of the hexagonal phase at room temperature. It seems possible that the strained orthorhombic $MgRbPO_4 \cdot 6H_2O$ may exist in the hexagonal form at higher temperatures or with partial substitution of Cs^+ for Rb^+ ions.

Registry No. $MgNH_4PO_4 \cdot 6H_2O$, 13478-16-5; $MgCsPO_4 \cdot 6H_2O$, 54774-72-0; $MgKPO_4 \cdot 6H_2O$, 19004-04-7; $MgRbPO_4 \cdot 6H_2O$, 54774-73-1; $MgTlPO_4 \cdot 6H_2O$, 54774-74-2; struvite, 15490-91-2.

References and Notes

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(2) (a) Abstracted in part from a dissertation submitted by R. Chianelli to the Department of Chemistry, Polytechnic Institute of New York, in partial fulfillment of the requirements for the Ph.D. degree, June 1974. (b) Abstracted in part from a thesis submitted by R. Korenstein to the Department of Chemistry, Polytechnic Institute of New York, in partial fulfillment of the requirements for the B.S. degree, June 1973.
(3) C. Palache, H. Berman, and C. Frondel, "Dana's System of Mineralogy", Vol. II, 1951, pp 715–717.
(4) J. A. Bland and S. J. Basinski, *Nature (London)*, **183**, 1385 (1959).
(5) A. Whitaker and A. W. Jeffery, *Acta Crystallogr., Sect. B*, **26**, 1429 (1970).
(6) A. Whitaker and A. W. Jeffery, *Acta Crystallogr., Sect. B*, **25**, 1440 (1970).
(7) J. R. Lehr, E. H. Brown, A. W. Frazier, J. P. Smith, and R. D. Thrasher, *Tenn. Val. Auth., Chem. Eng. Bull.*, **No. 6** (1967).
(8) B. Dickens and W. E. Brown, *Acta Crystallogr., Sect. B*, **25**, 1159 (1972).
(9) A. Ferrari, L. Cavalca, and M. Nardelli, *Gazz. Chim. Ital.*, **85**, 169 (1955).
(10) A. Ferrari, L. Cavalca, and M. Nardelli, *Gazz. Chim. Ital.*, **85**, 1232 (1955).
(11) E. Banks, R. Chianelli, and F. Pintchovsky, *J. Cryst. Growth*, **18**, 195 (1973).
(12) E. Banks and R. Chianelli, *J. Appl. Crystallogr.*, **7**, 301 (1974).
(13) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, pp 17–19.
(14) R. C. Plumb and D. F. Hornig, *J. Chem. Phys.*, **21**, 366–367 (1953).
(15) H. A. Levy and S. W. Peterson, *J. Chem. Phys.*, **21**, 366 (1953).

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Single-Crystal Polarized Electronic Spectra of the Pentakis(2-picoline *N*-oxide)cobalt(II) Perchlorate Complex

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Single-crystal polarized electronic spectra of the pentakis(2-picoline *N*-oxide)cobalt(II) perchlorate complex, $[Co(C_6H_7NO)_5](ClO_4)_2$, have been recorded for a crystal modification, the structure of which has been determined. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions a = 10.223 (3) Å, b = 9.659 (3) Å, c = 38.195 (12) Å, β = 107.92 (3)°, and Z = 4. The structure was refined to an R factor of 0.076. Assignment of the transitions on the basis of a C_{2v} symmetry is proposed and the energies of the electronic levels are discussed in terms of ligand field and angular overlap parameters.

Introduction

In the framework of a research program based on single-crystal spectra tending to test the validity of ligand field models for low-symmetry chromophores[1-3] it seemed interesting to investigate the pentakis(2-picoline *N*-oxide)cobalt(II) perchlorate complex[4] (CoO_5) which is reported to be approximately trigonal bipyramidal.[5] The fact that the donor atoms are five oxygens belonging to five equal ligands should simplify the problem of interpreting the spectra and should therefore give more information on the ligand ability of pyridine