

**NaMn<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) and  
KCd<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>)****J. Bennazha,<sup>a,b</sup> A. El-Maadi,<sup>a,c</sup> Ali Boukhari<sup>a</sup> and  
Elizabeth M. Holt<sup>d\*</sup>**

<sup>a</sup>Laboratoire de Chimie du Solide Appliqué, Laboratoire Associé Francophone N° 501, Université Mohammed V, Agdal, Av. Ibn Batouta, BP 1014, Rabat, Morocco, <sup>b</sup>Département de Chimie, Faculté des Sciences et Techniques, Université Hassan-II, Mohammedia, Morocco, <sup>c</sup>Laboratoire de Physico-Chimie des Matériaux, Département de Chimie, Faculté des Sciences de Kénitra, Université Ibn Tofail, Kenitra, Morocco, and <sup>d</sup>Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA  
Correspondence e-mail: betsy@biochem.okstate.edu

Received 11 March 2002

Accepted 15 April 2002

Online 11 May 2002

The crystal structures of two new diphosphates, sodium hexamanganese bis(diphosphate) triphosphate, NaMn<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>), and potassium hexacadmium bis(diphosphate) triphosphate, KCd<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>), confirm the rigidity of the M<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) matrix (*M* is Mn or Cd) and the relatively fixed dimensions of the tunnels extending in the *a* direction of the unit cell. The compounds are isomorphous; the P<sub>2</sub>O<sub>7</sub><sup>4-</sup> anion and the alkali metal cations lie on mirror planes. Bond-valence analysis of the bonding details of the atoms found within the tunnels permits a prediction of the conductivity.

**Comment**

Extending our studies of transition metal phosphate complexes (Bennazha *et al.*, 1999; Erragh *et al.*, 1998*a,b*; Eddahby *et al.*, 1997; Amroussi *et al.*, 1997) of the formula AB(P<sub>2</sub>O<sub>7</sub>) into stoichiometries of greater complexity, we have recently reported the single-crystal X-ray structures of two compounds of stoichiometry A<sup>I</sup>B<sup>II</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>), with *A* = K and *B* = Mn, and *A* = Ag and *B* = Mn (Bennazha *et al.*, 2001), a family of compounds previously observed only with *A* = NH<sub>4</sub><sup>+</sup> [(NH<sub>4</sub>)Cd<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>); Ivanov *et al.*, 1978]. We have now identified two further members of this family, namely NaMn<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>), (I), and KCd<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>), (II).

These two complexes contain a mixture of the phosphate moieties P<sub>2</sub>O<sub>7</sub> and P<sub>3</sub>O<sub>10</sub>, which is highly unusual (Durif, 1995). There are only two other examples of triphosphate, P<sub>3</sub>O<sub>10</sub><sup>5-</sup>, and diphosphate, P<sub>2</sub>O<sub>7</sub><sup>4-</sup>, existing in the same unit cell, namely Na<sub>7</sub>Y<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) (Hamady & Jouini, 1996) and Ca<sub>3</sub>(NH<sub>4</sub>)<sub>4</sub>H<sub>3</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) (Actina *et al.*, 1989).

Structures (I) and (II) are isomorphous with those of the previously reported A<sup>I</sup>B<sup>II</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) compounds, with *A* = K and *B* = Mn, and *A* = Ag and *B* = Mn (Bennazha *et al.*, 2001), and with (NH<sub>4</sub>)Cd<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) (Ivanov *et al.*, 1978).

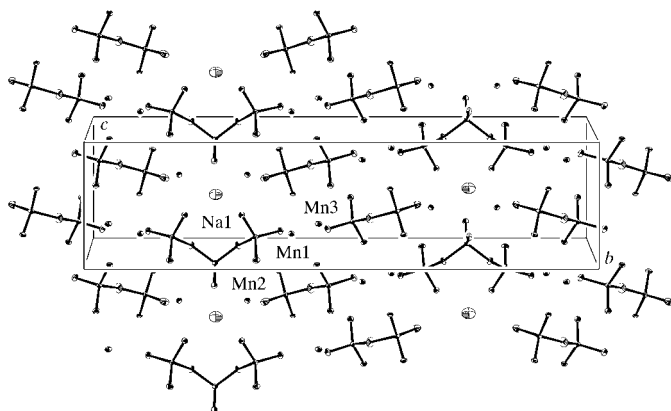
Members of this family crystallize with layers of P<sub>2</sub>O<sub>7</sub><sup>4-</sup> groups alternating with P<sub>3</sub>O<sub>10</sub><sup>5-</sup> layers along the *b* axis (Fig. 1). The *A* atoms (K, Na or Ag) are found between P<sub>3</sub>O<sub>10</sub> groups, and the Mn or Cd atoms are seen within and at the edges of the P<sub>2</sub>O<sub>7</sub> layers. The *A* atom is located on a mirror plane and displays tenfold coordination geometry. It is seen to occupy a tunnel extending parallel to the shortest cell dimension.

Knowledge of these two additional structures provides the opportunity to make several comparisons. Firstly, one can examine the structures of the A<sup>I</sup>Mn<sub>6</sub><sup>II</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) series, with *A* = K, Ag or Na, to ascertain the influence of the difference in the size of *A* upon the structure as a whole. In this series, the ionic radii decrease in the following order: K 1.59, Ag 1.28 and Na 1.24 Å (Shannon, 1976). The cell volumes show an irregular decrease in the order 925.1 (9), 928 (2) and 891.1 (3) Å<sup>3</sup>. Within the series, the calculated densities, 3.481, 3.716 and 3.553 Mg m<sup>-3</sup>, and the average *A*—O distances for the ten-coordinate *A* atom, 3.027 (3), 2.997 (9) and 2.955 (6) Å, differ only marginally. Thus, one asks how the other atoms accommodate the change in the radius of the *A* atom. Potentially, changes might be observed in the conformation of the phosphate groups or in the Mn bonding.

The P<sub>2</sub>O<sub>7</sub> groups show no change in conformation: the O—P···P—O torsion angles are 60.0, 59.5 and 60.0°. The P—O—P angles are 150.3 (2), 151.4 (6) and 153.1 (3)°, respectively. Similarly, the P<sub>3</sub>O<sub>10</sub> groups are identical within experimental error: the P—P—P angles are 93.7 (2), 93.2 (7) and 93.8 (3)°, and the O—P—P—O torsion angles have averages of 3.26, 4.36 and 3.3°, respectively. The details of the Mn bonding are similar; the pseudo-octahedral Mn atom has average Mn—O distances of 2.22 (3), 2.22 (8) and 2.195 (4) Å in the three structures, respectively.

While previous work has led us to the idea that differences in the ratios of the ionic radii of the *A* and *B* atoms lead to very clear differences in structure in A<sup>I</sup>B<sup>II</sup>P<sub>2</sub>O<sub>7</sub>-type diphosphate structures (Elmarzouki, 2002), this appears not to be the case in A<sup>I</sup>B<sup>II</sup>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) structures. One concludes that the Mn<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) matrix is rigid and provides a rigid host matrix into which has been inserted the K, Ag or Na cation. The Mn<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) matrix is analogous to the zeolite-type matrices, which are rigid and resist conformational changes due to the presence of guest atoms or molecules in their cavities. Indeed, a projection view of NaMn<sub>6</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(P<sub>3</sub>O<sub>10</sub>) down the shortest axis (*a*) clearly shows that the *A* atoms lie in the tunnel (Fig. 1).

Bond-valence analysis (Brown, 1981) is usually applied to verify the identity of an atom in a structure, the charge resident on an atom or the quality of a structure determination. However, in our hands, it has proved a useful means of identifying potential atomic movement or conductivity. Cations which are well fixed in their sites will display bond-valence totals approximately equal to their oxidation states. Atoms which are potentially mobile will have lesser totals, indicating their lesser degree of interaction with their neighbors and thus their mobility. The totals for the ten-coordinate *A* atoms K, Ag and Na are 1.015, 0.670 and 0.699, respectively. These large deviations from 1.0 may be interpreted in two


**Figure 1**

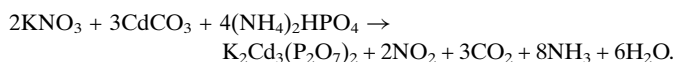
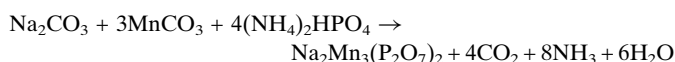
A projection view of  $\text{NaMn}_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  down the  $a$  axis. Displacement ellipsoids are shown at the 50% probability level. The  $\text{KCd}_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  compound is isomorphous.

ways. One suspects that the Ag and Na structures will show significant conductivity in the  $a$  direction as the  $A$  atoms move in that direction along the tunnels. Secondly, the  $\text{Mn}_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  matrix has not collapsed or adapted itself in any significant way to permit higher degrees of interaction with the  $A$  atom. This attests to the rigidity of this structure, in which the  $A$  atom is a guest.

The preparation of  $\text{KCd}_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  provides the opportunity to compare  $\text{KMn}_6$  and  $\text{KCd}_6$ , to see what difference the change in the identity of  $B$  makes in the rigidity of the structure formed by  $B_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$ . The ionic radius of Cd is slightly larger than that of Mn (Mn 0.67 Å and Cd 0.95 Å). Details of the  $B_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  framework of the two structures, with  $A = \text{K}$  and  $B = \text{Mn}$  or  $\text{Cd}$ , are nearly identical within experimental error; the average  $B\text{—O}$  distances for the two structures are 2.22 (3) and 2.283 (4) Å, respectively. In the  $\text{P}_2\text{O}_7$  groups, the  $\text{O—P—P—O}$  torsion angles average 60.0 and 59.2°, with  $\text{P—O—P}$  angles of 150.3 (2) and 154.1 (6)°, respectively. The  $\text{P}_3\text{O}_{10}$  groups display  $\text{O—P—P—O}$  torsion angles of 3.26 and 4.5°, with  $\text{P—P—P}$  angles of 93.7 (2) and 92.6 (2)°, respectively. Furthermore, the average  $\text{K—O}$  bond distances for ten-coordinate K are 3.027 (3) and 3.061 (5) Å, with bond-valence totals of 1.015 and 1.177, respectively. Thus, the substitution of Cd for Mn in the  $B_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$  framework has made little difference in the structural details of the framework and in the environment experienced by the guest K ion.

## Experimental

The starting materials  $\text{Na}_2\text{CO}_3$  [for (I)] or  $\text{KNO}_3$  [for (II)],  $\text{MnCO}_3$  (or  $\text{CdCO}_3$ ) and  $(\text{NH}_4)_2\text{HPO}_4$  were mixed in a stoichiometry expected to lead to the preparation of  $A_2B_3(\text{P}_2\text{O}_7)_2$ , with  $A = \text{Na}$  and  $B = \text{Mn}$  for (I), and  $A = \text{K}$  and  $B = \text{Cd}$  for (II), according to the following two reactions:



The starting mixture was heated slowly to 873 K to eliminate  $\text{NH}_3$ ,  $\text{CO}_2$  [and  $\text{NO}_2$  in (II)] and  $\text{H}_2\text{O}$ , followed by heating to 1223 K [for (I)] or 1023 K [for (II)] and slow cooling (6 K h<sup>-1</sup>) to 673 K, whereupon the furnace was allowed to cool to ambient temperature without control. Colorless crystalline solids were obtained.

## Compound (I)

### Crystal data

$\text{NaMn}_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$   
 $M_r = 953.42$   
 Monoclinic,  $P2_1/m$   
 $a = 5.345$  (1) Å  
 $b = 26.620$  (4) Å  
 $c = 6.559$  (1) Å  
 $\beta = 107.28$  (1)°  
 $V = 891.1$  (3) Å<sup>3</sup>  
 $Z = 2$

$D_x = 3.553$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 27 reflections  
 $\theta = 7.5\text{--}10.2^\circ$   
 $\mu = 4.91$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Chunk, colorless  
 0.1 × 0.1 × 0.1 mm

### Data collection

Syntax  $P4$  four-circle diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  $\psi$  scan  
 (XEMP; Siemens, 1991)  
 $T_{\min} = 0.582$ ,  $T_{\max} = 0.612$   
 3530 measured reflections  
 2645 independent reflections  
 1822 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.051$   
 $\theta_{\text{max}} = 30^\circ$   
 $h = -1 \rightarrow 7$   
 $k = -1 \rightarrow 37$   
 $l = -9 \rightarrow 9$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.050$   
 $wR(F^2) = 0.088$   
 $S = 1.03$   
 2645 reflections  
 179 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0065P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.08$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.10$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.0016 (3)

**Table 1**

Selected interatomic distances (Å) for (I).

Na1—O23	2.441 (5)	Mn2—O33 <sup>v</sup>	2.075 (4)
Na1—O33 <sup>i</sup>	3.111 (5)	Mn2—O23	2.120 (3)
Na1—O14 <sup>ii</sup>	3.264 (5)	Mn2—O32 <sup>iv</sup>	2.164 (4)
Na1—O21	3.322 (5)	Mn2—O21	2.173 (3)
Na1—O13 <sup>iii</sup>	2.694 (6)	Mn2—O13	2.263 (3)
Na1—O11 <sup>iii</sup>	2.579 (6)	Mn2—O11 <sup>ii</sup>	2.334 (4)
Mn1—O32 <sup>iv</sup>	2.134 (3)	Mn3—O43 <sup>vii</sup>	2.119 (4)
Mn1—O22 <sup>ii</sup>	2.136 (4)	Mn3—O42 <sup>viii</sup>	2.139 (4)
Mn1—O31 <sup>i</sup>	2.171 (3)	Mn3—O31 <sup>i</sup>	2.157 (4)
Mn1—O41 <sup>v</sup>	2.181 (4)	Mn3—O41 <sup>v</sup>	2.158 (3)
Mn1—O42	2.204 (4)	Mn3—O22	2.293 (4)
Mn1—O21	2.293 (4)	Mn3—O43	2.411 (4)

Symmetry codes: (i)  $1 - x, 1 - y, 1 - z$ ; (ii)  $1 + x, y, z$ ; (iii)  $1 + x, y, 1 + z$ ; (iv)  $1 - x, 1 - y, -z$ ; (v)  $-x, 1 - y, -z$ ; (vi)  $x, y, z - 1$ ; (vii)  $-x, 1 - y, 1 - z$ ; (viii)  $x - 1, y, z$ .

## Compound (II)

### Crystal data

$\text{KCd}_6(\text{P}_2\text{O}_7)_2(\text{P}_3\text{O}_{10})$   
 $M_r = 1314.29$   
 Monoclinic,  $P2_1/m$   
 $a = 5.479$  (1) Å  
 $b = 27.112$  (6) Å  
 $c = 6.769$  (1) Å  
 $\beta = 107.11$  (2)°  
 $V = 961.0$  (3) Å<sup>3</sup>  
 $Z = 2$

$D_x = 4.542$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 19 reflections  
 $\theta = 4.3\text{--}11.4^\circ$   
 $\mu = 7.45$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Chunk, colorless  
 0.1 × 0.1 × 0.1 mm

## Data collection

Syntax P4 four-circle diffractometer	$R_{\text{int}} = 0.061$
$\theta/2\theta$ scans	$\theta_{\text{max}} = 30^\circ$
Absorption correction: $\psi$ scan (XEMP; Siemens, 1991)	$h = -7 \rightarrow 1$
$T_{\text{min}} = 0.422$ , $T_{\text{max}} = 0.475$	$k = -1 \rightarrow 38$
3802 measured reflections	$l = -9 \rightarrow 9$
2866 independent reflections	3 standard reflections
2575 reflections with $I > 2\sigma(I)$	every 97 reflections intensity decay: none

## Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R(F) = 0.040$	$\Delta\rho_{\text{max}} = 0.03 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.124$	$\Delta\rho_{\text{min}} = -0.02 \text{ e } \text{\AA}^{-3}$
$S = 1.01$	Extinction correction: <i>SHELXL97</i> (Sheldrick, 1997)
2866 reflections	Extinction coefficient: 0.0312 (14)
179 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

**Table 2**

Selected interatomic distances (Å) for (II).

Cd1—O32 <sup>i</sup>	2.219 (4)	Cd3—O43 <sup>vi</sup>	2.228 (4)
Cd1—O22 <sup>ii</sup>	2.228 (4)	Cd3—O42 <sup>vii</sup>	2.229 (4)
Cd1—O31 <sup>iii</sup>	2.263 (4)	Cd3—O31 <sup>iii</sup>	2.250 (4)
Cd1—O41 <sup>iv</sup>	2.286 (4)	Cd3—O41 <sup>iv</sup>	2.265 (4)
Cd1—O42	2.291 (4)	Cd3—O22	2.410 (4)
Cd1—O21	2.359 (4)	Cd3—O43	2.416 (4)
Cd2—O33 <sup>iv</sup>	2.189 (5)	K1—O23	2.763 (5)
Cd2—O23 <sup>v</sup>	2.207 (4)	K1—O13 <sup>viii</sup>	2.875 (6)
Cd2—O32 <sup>i</sup>	2.234 (4)	K1—O11 <sup>viii</sup>	2.983 (6)
Cd2—O21	2.302 (4)	K1—O14 <sup>ix</sup>	3.058 (4)
Cd2—O13	2.335 (3)	K1—O21	3.261 (4)
Cd2—O11 <sup>ii</sup>	2.403 (3)	K1—O33 <sup>iii</sup>	3.296 (6)

Symmetry codes: (i)  $1-x, 1-y, -z$ ; (ii)  $1+x, y, z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $-x, 1-y, -z$ ; (v)  $x, y, z-1$ ; (vi)  $-x, 1-y, 1-z$ ; (vii)  $x-1, y, z$ ; (viii)  $1+x, y, 1+z$ ; (ix)  $1+x, \frac{1}{2}-y, z$ .

For both compounds, data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1364). Services for accessing these data are described at the back of the journal.

## References

- Actina, L., Dindune, A., Vaivada, M. & Konstant, Z. A. (1989). *Latv. PSR Zinat. Akad. Vestis Kim. Ser.* **6**, 683–687.
- Amroussi, F., Moqine, A., Boukhari, A. & Holt, E. M. (1997). *Eur. J. Solid State Inorg. Chem.* **34**, 161–168.
- Bennazha, J., Boukhari, A. & Holt, E. M. (1999). *Solid State Sci.* **1**, 373–380.
- Bennazha, J., El-Maadi, A., Boukhari, A. & Holt, E. M. (2001). *J. Solid State Sci.* **3**, 587–592.
- Brown, I. D. (1981). *Struct. Bonding Cryst.* **2**, 1–13.
- Durif, A. (1995). *Crystal Chemistry of Condensed Phosphates*, pp. 353–354. New York: Plenum Press.
- Eddahby, L., Berrada, A., Boukhari, A. & Holt, E. M. (1997). *Eur. J. Solid State Inorg. Chem.* **34**, 527–551.
- Elmarzouki, A. (2002). Thèse d'Etat, Université Mohammed V, Rabat, Morocco.
- Erragh, F., Boukhari, A., Sadel, A. & Holt, E. M. (1998a). *Acta Cryst.* **C54**, 1373–1376.
- Erragh, F., Boukhari, A., Sadel, A. & Holt, E. M. (1998b). *Acta Cryst.* **C54**, 1746–1747.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Hamady, A. & Jouini, T. (1996). *Z. Anorg. Allg. Chem.* **622**, 1987–1990.
- Ivanov, Y. A., Simonov, M. A. & Belov, N. V. (1978). *Dokl. Akad. Nauk SSSR*, **242**, 599–602.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1991). *XEMP* (Version 4.2) and *XSCANS User's Manual* (Version 2.10b). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.