

site occupancies was attempted. However, this influenced neither the displacement parameters nor the *R* values. In an attempt to resolve the sixfold disorder, the structure was recalculated based on a triplet of a monoclinic unit cell (*a* = 9.814, *b* = 7.634, *c* = 12.445 Å,  $\beta$  = 108.14°, *Z* = 2) in space group *I*2/*m* (*t* subgroup of *R*3*m*). The transformation matrix is  $-\frac{1}{3}, \frac{1}{3}, \frac{1}{3} / 1, 1, 0 / -\frac{1}{6}, \frac{1}{6}, -\frac{1}{3}$  and the matrix of threefold rotation (twinning element) is 0, 1, 0 / -1, -1, 0 / 0, 0, 1. However, the refinement did not stabilize and one Cl ion of the YbCl<sub>6</sub> octahedron showed strongly anisotropic displacement parameters. A further attempt involved refinement as an inversion twin in the space group *Im*. Anisotropic refinement gave *R*1 = 0.036 for 1274 reflections with *I* < 2σ(*I*) and *wR*2(all data) = 0.092. The ratio of the triplets was 34(21 + 13):32(30 + 2):34(5 + 29), with the ratios of inversion twins in parentheses. However, the displacement parameters became even more anisotropic and the YbCl<sub>6</sub> octahedron showed an elongation that we could not rationalize. Furthermore, the *R* values are no better than in the rhombohedral model. We therefore believe that disorder rather than twinning gives a correct model of the structure.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *PROCESS*, *PSISCAN* and *PSICALC* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994), *SCHAKAL92* (Keller, 1993). Software used to prepare material for publication: *SHELXL93*.

We thank Professor H.-J. Seifert for support and dedicate this paper to him on the occasion of his last 'first fine day'.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Sr<sub>4</sub>Ga<sub>3</sub>Mo<sub>26</sub>O<sub>48</sub> Containing Mo<sub>7</sub> Clusters and Infinite Mo<sub>7</sub>–Mo<sub>10</sub>–Mo<sub>7</sub> Chains

J. TORTELIER AND P. GOUGEON

*Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA CNRS No. 1495, Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes CEDEX, France*

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### Abstract

The crystal structure of the strontium gallium molybdate Sr<sub>4</sub>Ga<sub>3</sub>Mo<sub>26</sub>O<sub>48</sub> is characterized by quasi-isolated monocapped octahedral Mo<sub>7</sub> clusters and infinite Mo chains arranged in layers parallel to the *ac* plane of the monoclinic unit cell. The repeat unit of the chains is the tricluster Mo<sub>24</sub> chain fragment consisting of one Mo<sub>10</sub> and two Mo<sub>7</sub> clusters. The Mo—Mo distances range between 2.584 (1) and 2.786 (1) Å in the Mo<sub>7</sub> clusters and between 2.5963 (9) and 2.938 (1) Å in the chains. The shortest Mo—Mo distance between Mo<sub>7</sub> clusters is 3.1575 (9) Å and between Mo<sub>7</sub> clusters and the chains is 3.171 (1) Å, which excludes any direct Mo—Mo interactions. The Mo—O distances range from 1.922 (6) to 2.163 (6) Å, as usually observed in reduced Mo oxides. The four crystallographically independent Sr<sup>2+</sup> ions have coordination numbers of 11 or 12 with an environment in each case based upon a distorted cuboctahedron. The Sr—O distances range from 2.495 (6) to 3.105 (5) Å. The Ga<sup>3+</sup> ions are approximately tetrahedrally or octahedrally coordinated by O atoms. The Ga—O distances vary between 1.902 (6) and 2.059 (6) Å for the octahedral sites, and between 1.830 (5) and 1.873 (6) Å for the tetrahedral site.

### Comment

Over the last two decades, numerous reduced molybdenum oxides have been synthesized by solid-state reaction and fused-salt electrolysis. Most of these compounds contain clusters, sheets or infinite chains of Mo atoms with strong metal–metal bonds. Until now, only sheets based on Mo<sub>3</sub> triangles were known, while infinite chains can be based on digonal Mo<sub>2</sub> groups, Mo<sub>4</sub> rhomboids or on octahedral Mo<sub>6</sub> clusters. Although the latter cluster has only been obtained in the unique compound Ca<sub>16.5</sub>Mo<sub>13.5</sub>O<sub>40</sub> (Lindblom & Strandberg, 1989) so far, it also constitutes the basic building block of larger clusters such as Mo<sub>4*n*+2</sub> (*n* = 2, 3, 4 and 5) (Hibble, Cheetham, Bogle, Wakerley & Cox, 1988; Mat-tausch, Simon & Peters, 1986; Dronskowski & Simon, 1989; Schimek & McCarley, 1994) by sharing its *trans* edges. The final stage of this process of condensa-

tion of Mo<sub>6</sub> clusters *via trans* edges is the infinite chain  $[\text{Mo}_{4/2}\text{Mo}_2]_{\infty}$  which occurs, for example, in the  $M_7\text{Mo}_4\text{O}_6$  series ( $M = \text{Na}, \text{K}, \text{Rb}, \text{Sr}, \text{Ba}, \text{Sn}, \text{Pb}, \text{In}$ ) (Torardi & McCarley, 1979, 1981; McCarley, 1986). Recently, two novel clusters, namely the Mo<sub>8</sub> cluster and the tricluster Mo<sub>24</sub> chain fragment, were obtained in the two series of compounds  $R\text{Mo}_8\text{O}_{14}$  ( $R = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$  and  $\text{Sm}$ ) (Leligny, Ledesert, Labbe, Raveau & McCarroll, 1990; Leligny *et al.*, 1993; Gougeon & McCarley, 1991; Kerihuel & Gougeon, 1995*a,b*) and  $R_5\text{Mo}_{32}\text{O}_{54}$  ( $R = \text{La}, \text{Ce}, \text{Pr}$  and  $\text{Nd}$ ) (Gall, Toupet & Gougeon, 1993), respectively. The former cluster is based on an octahedral Mo<sub>6</sub> cluster, two faces of which are capped by two additional Mo atoms. This cluster, which exists in the  $R\text{Mo}_8\text{O}_{14}$  family in two different forms (*cis* and *trans* configuration) of the three possible isomers, is, to our knowledge, the first example of geometrical isomerism observed in reduced molybdenum compounds in solid-state chemistry. The Mo core of the remarkably chain-like Mo<sub>24</sub>O<sub>60</sub> cluster unit observed in the second series consists of one bioctahedral Mo<sub>10</sub> and two monocapped Mo<sub>7</sub> clusters strongly linked through a Mo—Mo bond of 2.77 Å. We present here the crystal structure of  $\text{Sr}_4\text{Ga}_3\text{Mo}_{26}\text{O}_{48}$ , where the tricluster Mo<sub>7</sub>—Mo<sub>10</sub>—Mo<sub>7</sub> chain fragments form infinite complex chains which coexist with quasi-isolated monocapped octahedral Mo<sub>7</sub> clusters.

Fig. 1, which represents the projection of the Mo network for  $\text{Sr}_4\text{Ga}_3\text{Mo}_{26}\text{O}_{48}$  on the *ac* plane, clearly shows that the main metallic building blocks of this structure are monocapped octahedral Mo<sub>7</sub> clusters and infinite Mo chains, which are both arranged in layers parallel to the *ac* plane. The repeat unit of the chains, which run parallel to the *a* axis, is the tricluster Mo<sub>24</sub> chain fragment shown in Fig. 2 with its oxygen environment. This fragment, which consists of one Mo<sub>10</sub> and two Mo<sub>7</sub> clusters strongly linked through an Mo—Mo bond, differs slightly from the one previously observed in  $\text{La}_5\text{Mo}_{32}\text{O}_{54}$ , where the capped face is the one defined by Mo(16), Mo(18) and Mo(20) in Fig. 2. The construction of the chain in  $\text{Sr}_4\text{Ga}_3\text{Mo}_{26}\text{O}_{48}$  arises from the sharing of  $\text{O}^i \cdots \text{O}^i$  edges accompanied by  $\text{O}^{a-i}$  bonds, as shown in Fig. 2. This new type of connection results in an Mo(18)—Mo(18) distance of 2.780(1) Å between the Mo<sub>7</sub> clusters of the tricluster chain fragments. In  $\text{La}_5\text{Mo}_{32}\text{O}_{54}$ , they are separated from each other by 3.1468(9) Å. Within the Mo<sub>7</sub> clusters of the Mo<sub>24</sub> chain fragment, the Mo—Mo distances lie between 2.616(1) and 2.938(1) Å, in contrast to 2.5561(9)—2.7925(9) Å in  $\text{La}_5\text{Mo}_{32}\text{O}_{54}$ . The average Mo—Mo distance is 2.742 Å as opposed to 2.710 Å in  $\text{La}_5\text{Mo}_{32}\text{O}_{54}$ . This larger value probably results from a diminution of the number of electrons on the Mo<sub>7</sub> cluster due to an electron transfer towards the Mo(18)—Mo(18), Mo(18)—Mo(20) and Mo(16)—Mo(18) intercluster bonds between the Mo<sub>7</sub> clusters of the Mo<sub>24</sub> chain fragments. The Mo—O bond distances vary from 1.984(6) to

2.156(6) Å with an average distance of 2.070 Å. For the Mo<sub>10</sub> cluster, which consists of two distorted Mo<sub>6</sub> octahedra sharing an edge, the Mo—Mo distances range between 2.5963(9) and 2.8478(9) Å. The average Mo—Mo distance of 2.744 Å is similar to that calculated for the  $M\text{Mo}_5\text{O}_8$  compounds containing divalent cations where the Mo<sub>10</sub> clusters form infinite chains [2.736 Å in  $\text{CaMo}_5\text{O}_8$  (Gougeon, 1993), 2.742 Å in  $\text{SrMo}_5\text{O}_8$  (Gall & Gougeon, 1994), 2.740 Å in  $\text{EuMo}_5\text{O}_8$  (Gall, 1993), 2.746 Å in  $\text{SnMo}_5\text{O}_8$  (Gougeon, Potel & Sergent, 1990) and 2.745 Å in  $\text{PbMo}_5\text{O}_8$  (Dronskowski & Simon, 1989; Dronskowski, Simon & Mertin, 1991)]. The Mo—O distances spread over a wide range [1.930(6)—2.157(6) Å] with an average value of 2.063 Å, which also corresponds to that found in the  $M\text{Mo}_5\text{O}_8$  compounds where  $M = \text{Ca}^{2+}$  (2.064 Å),  $\text{Sr}^{2+}$  (2.064 Å),  $\text{Eu}^{2+}$  (2.063 Å),  $\text{Sn}^{2+}$  (2.064 Å) and  $\text{Pb}^{2+}$  (2.061 Å). In the  $R^{3+}\text{Mo}_5\text{O}_8$  compounds, the average values range from 2.074 to 2.078 Å. The shortest intercluster distance between the Mo<sub>7</sub> and the Mo<sub>10</sub> cluster is 2.7816(9) Å [Mo(21)—Mo(22)], slightly longer than the value of 2.7688(9) Å in  $\text{La}_5\text{Mo}_{32}\text{O}_{54}$ . The other four intercluster distances range between 2.982(1) [Mo(20)—Mo(22)] and 3.059(1) Å [Mo(21)—Mo(23)], while in  $\text{La}_5\text{Mo}_{32}\text{O}_{54}$  they range from 2.9916(9) to 3.0637(9) Å.

The second novel feature of the title compound is the presence of monocapped octahedral Mo<sub>7</sub> clusters (Fig. 3). Indeed, although  $M_7$  clusters are known in metal—organic compounds with  $M = \text{Ru}, \text{Re}, \text{Os}$  and  $\text{Ir}$ , for example, it is the first time that such clusters have been encountered in an inorganic compound. The

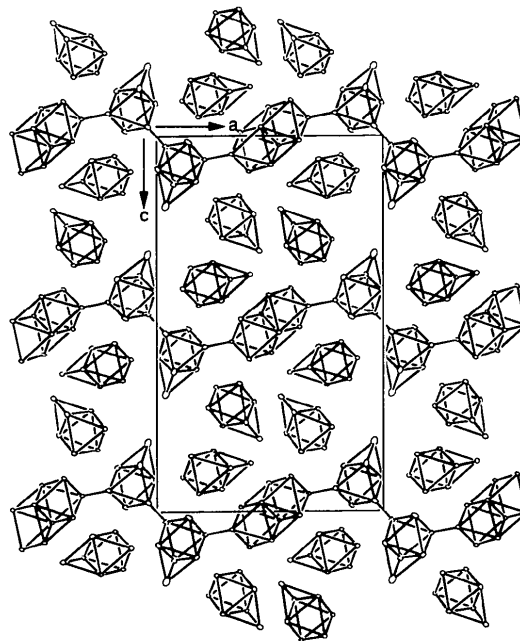


Fig. 1. Projection of  $\text{Sr}_4\text{Ga}_3\text{Mo}_{26}\text{O}_{48}$  on the *ac* plane showing only the molybdenum network. Displacement ellipsoids are drawn at the 95% probability level.

Mo—Mo distances within the two crystallographically independent monocapped Mo<sub>7</sub> clusters lie between 2.584(1) and 2.7798(9) Å for the cluster formed by the Mo atoms numbered from 1 to 7 (cluster I) and between 2.610(1) and 2.786(1) Å for the cluster formed by the Mo atoms numbered from 8 to 14 (cluster II). The average Mo—Mo distances for these two clusters are 2.707 and 2.716 Å, respectively. The Mo—O bond distances are in the ranges 1.922(6)–2.163(6) Å and 1.925(6)–2.157(6) Å with average values of 2.045 and 2.043 Å, respectively. The shortest Mo—Mo distance between the quasi-isolated Mo<sub>7</sub> clusters is 3.1575(9) Å [Mo(1)—Mo(11)] and between the Mo<sub>7</sub> clusters and the chains is 3.171(1) Å [Mo(8)—Mo(25)], which excludes any direct Mo—Mo interactions.

Of the four crystallographically independent Sr<sup>2+</sup> ions (which are all in general positions), Sr(1), Sr(2) and Sr(3) are surrounded by twelve O atoms forming a distorted cuboctahedron. The Sr—O distances range

from 2.513(6) to 3.000(6) Å for the Sr(1) site, from 2.495(6) to 3.008(6) Å for the Sr(2) site and from 2.640(6) to 3.105(5) Å for the Sr(3) site. The Sr(4) ions occupy twinned cavities formed by two fused cuboctahedra and are surrounded by eleven O atoms at distances varying from 2.557(5) to 3.095(5) Å. The Ga<sup>3+</sup> ions are approximately tetrahedrally [Ga(3)] or octahedrally [Ga(1) and Ga(2)] coordinated by O atoms. The Ga—O distances are in the range 1.909(6)–2.055(6) Å and 1.902(6)–2.059(6) Å for the Ga(1) and Ga(2) octahedral sites, respectively, and between 1.830(5) and 1.873(6) Å for the tetrahedral site. The average Ga—O distances are 1.981 and 1.976 Å for the octahedral Ga(1) and Ga(2) sites and 1.848 Å for the tetrahedral site. These values are in good agreement with the distances expected from the sum of the ionic radii of O<sup>2-</sup> and Ga<sup>3+</sup> ions in octahedral (2.00 Å) and tetrahedral (1.85 Å) coordination according to Shannon & Prewitt (1969).

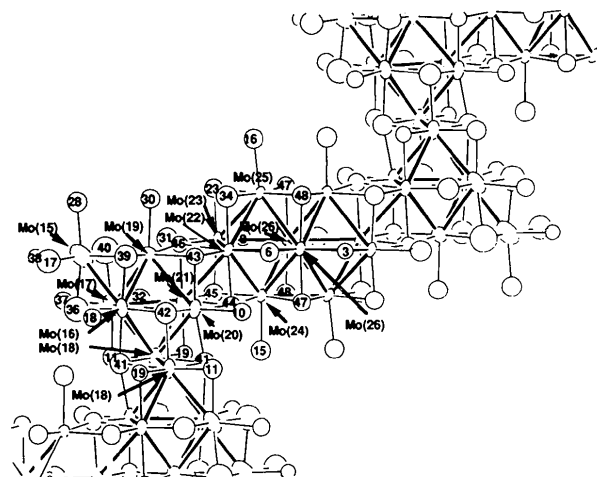


Fig. 2. A section of the tricluster Mo<sub>7</sub>–Mo<sub>10</sub>–Mo<sub>7</sub> chain. Only the shortest Mo—Mo bonds between the Mo<sub>7</sub> clusters and the Mo<sub>7</sub> and Mo<sub>10</sub> clusters are shown. An inversion centre lies at the middle of the Mo(26)—Mo(26) bond.

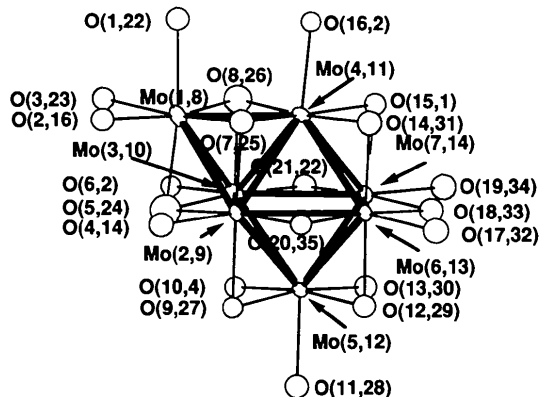


Fig. 3. The numbering scheme in the monocapped octahedral Mo<sub>7</sub>O<sub>21</sub> cluster units. The first numbers correspond to cluster I and the second to cluster II (see text).

## Experimental

Single crystals were obtained by mixing stoichiometric amounts of Eu<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub> and Mo, all in powder form. The mixture was pressed into a pellet and placed in a molybdenum crucible which was then sealed under a low argon pressure using an arc welding system. The mixture was heated at a rate of 300 K h<sup>-1</sup> to ca 1870 K, held at this temperature for 6 h, then heated up to 2220 K at 600 K h<sup>-1</sup> for 5 min and finally cooled at 100 K h<sup>-1</sup> down to 1400 K, the temperature at which the power was turned off.

### Crystal data

Sr<sub>4</sub>Ga<sub>3</sub>Mo<sub>26</sub>O<sub>48</sub>

*M<sub>r</sub>* = 3822.05

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 15.082(3) Å

*b* = 9.1900(3) Å

*c* = 26.499(5) Å

$\beta$  = 90.533(9)°

*V* = 3672.5(9) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 6.912 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25

reflections

$\theta$  = 8.1–18.0°

$\mu$  = 16.210 mm<sup>-1</sup>

*T* = 295 K

Irregular

0.19 × 0.12 × 0.04 mm

Black

### Data collection

Enraf–Nonius CAD-4

diffractometer

$\theta/2\theta$  scans

Absorption correction:

empirical (6  $\psi$  scans;

North, Phillips &

Mathews, 1968)

*T<sub>min</sub>* = 0.513, *T<sub>max</sub>* =

0.999

13 826 measured reflections

10 491 independent

reflections

7146 observed reflections

[*I* > 2 $\sigma$ (*I*)]

*R<sub>int</sub>* = 0.036

$\theta_{max}$  = 32°

*h* = 0 → 22

*k* = 0 → 13

*l* = -39 → 39

3 standard reflections

frequency: 90 min

intensity decay: <1%

*Refinement*

Refinement on *F*

*R* = 0.036

*wR* = 0.039

*S* = 1.325

7146 reflections

491 parameters

$w = 4F_o^2 / [\sigma^2(F_o^2)$

$+ 0.0009F_o^4]$

$(\Delta/\sigma)_{\max} < 0.01$

$$\Delta\rho_{\max} = 2.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -3.35 \text{ e } \text{\AA}^{-3}$$

Extinction correction: Stout & Jensen (1968)

Extinction coefficient:

$$1.09 (2) \times 10^{-8}$$

Atomic scattering factors from Cromer & Waber (1974)

O(25)	0.3867 (4)	0.2332 (7)	0.2599 (2)	0.57 (9)
O(26)	0.5063 (4)	0.5074 (7)	0.2522 (2)	0.78 (9)
O(27)	0.8199 (3)	0.0133 (6)	0.2171 (2)	0.42 (8)
O(28)	0.8901 (4)	0.2361 (7)	0.2645 (2)	0.54 (9)
O(29)	0.8501 (3)	-0.0036 (7)	0.3219 (2)	0.52 (9)
O(30)	0.7433 (4)	0.2509 (6)	0.3328 (2)	0.48 (9)
O(31)	0.3606 (4)	0.2397 (7)	0.1577 (2)	0.59 (9)
O(32)	0.1801 (4)	0.2508 (7)	0.1182 (2)	0.6 (1)
O(33)	0.7107 (3)	-0.0011 (7)	0.3880 (2)	0.55 (9)
O(34)	0.6035 (4)	0.2409 (7)	0.4075 (2)	0.62 (9)
O(35)	0.2164 (4)	0.2455 (6)	0.2252 (2)	0.44 (9)
O(36)	0.9614 (4)	0.4947 (7)	0.6456 (2)	0.84 (9)
O(37)	0.0344 (4)	0.2578 (6)	0.6928 (2)	0.43 (9)
O(38)	0.0040 (3)	0.0037 (6)	0.2438 (2)	0.29 (8)
O(39)	0.9227 (4)	0.2767 (7)	0.8745 (2)	0.73 (9)
O(40)	0.8553 (4)	-0.0062 (7)	0.8178 (2)	1.0 (1)
O(41)	0.9205 (3)	0.9958 (7)	0.0414 (2)	0.57 (9)
O(42)	0.9642 (4)	0.2520 (7)	0.4742 (2)	0.65 (9)
O(43)	0.7864 (4)	0.2429 (6)	0.9395 (2)	0.39 (9)
O(44)	0.7484 (3)	0.9991 (7)	0.0053 (2)	0.44 (8)
O(45)	0.3249 (4)	0.2422 (6)	0.0515 (2)	0.52 (9)
O(46)	0.7083 (3)	0.0018 (7)	0.8861 (2)	0.36 (8)
O(47)	0.6127 (3)	0.4979 (7)	0.5721 (2)	0.43 (8)
O(48)	0.4687 (4)	0.2762 (6)	0.9827 (2)	0.48 (9)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$B_{\text{iso}}$  for O atoms,  $B_{\text{eq}} = (4/3)\sum_i \beta_j a_i \cdot a_j$  for all others.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}/B_{\text{eq}}$
Mo(1)	0.58655 (4)	0.38126 (8)	0.12968 (2)	0.30 (1)
Mo(2)	0.24919 (4)	0.62050 (8)	0.83687 (2)	0.27 (1)
Mo(3)	0.28474 (4)	0.62240 (8)	0.93854 (2)	0.30 (1)
Mo(4)	0.32359 (4)	0.38213 (8)	0.88233 (2)	0.28 (1)
Mo(5)	0.11438 (4)	0.62044 (8)	0.90677 (2)	0.28 (1)
Mo(6)	0.14941 (4)	0.37802 (8)	0.85095 (2)	0.28 (1)
Mo(7)	0.18428 (4)	0.38023 (8)	0.95029 (2)	0.29 (1)
Mo(8)	0.45200 (4)	0.37677 (9)	0.30583 (3)	0.45 (1)
Mo(9)	0.28901 (4)	0.37950 (8)	0.27189 (2)	0.27 (1)
Mo(10)	0.39377 (4)	0.62300 (9)	0.26298 (3)	0.40 (1)
Mo(11)	0.42890 (4)	0.37737 (8)	0.20727 (2)	0.30 (1)
Mo(12)	0.22648 (4)	0.62042 (8)	0.22386 (2)	0.28 (1)
Mo(13)	0.26136 (4)	0.37626 (8)	0.16867 (2)	0.27 (1)
Mo(14)	0.36390 (4)	0.61772 (8)	0.15910 (2)	0.31 (1)
Mo(15)	0.04021 (5)	0.64271 (9)	0.68477 (3)	0.78 (1)
Mo(16)	0.00577 (4)	0.62443 (8)	0.58802 (3)	0.38 (1)
Mo(17)	0.07519 (4)	0.37678 (9)	0.62671 (3)	0.55 (1)
Mo(18)	0.03797 (4)	0.38241 (8)	0.52511 (3)	0.37 (1)
Mo(19)	0.17381 (4)	0.62387 (8)	0.62061 (3)	0.37 (1)
Mo(20)	0.13947 (4)	0.61672 (8)	0.51522 (3)	0.39 (1)
Mo(21)	0.21233 (4)	0.38503 (8)	0.56103 (2)	0.31 (1)
Mo(22)	0.32928 (4)	0.61563 (8)	0.54775 (2)	0.26 (1)
Mo(23)	0.59298 (4)	0.61345 (8)	0.40552 (2)	0.26 (1)
Mo(24)	0.36886 (4)	0.37364 (8)	0.48912 (2)	0.26 (1)
Mo(25)	0.50497 (4)	0.63245 (8)	0.57684 (2)	0.28 (1)
Mo(26)	0.46172 (4)	0.62361 (8)	0.47623 (2)	0.25 (1)
Sr(1)	0.22722 (5)	0.5032 (1)	0.39136 (3)	0.56 (1)
Sr(2)	0.33117 (5)	0.4966 (1)	0.72070 (3)	0.64 (1)
Sr(3)	0.11374 (6)	-0.0085 (1)	0.56290 (3)	1.22 (2)
Sr(4)	0.59749 (5)	0.5068 (1)	0.95915 (3)	0.76 (1)
Ga(1)	0.11256 (6)	0.1378 (1)	0.24194 (3)	0.42 (1)
Ga(2)	0.92023 (6)	0.3620 (1)	0.70342 (3)	0.41 (1)
Ga(3)	0.03472 (6)	0.0540 (1)	0.69414 (4)	0.48 (2)
O(1)	0.4665 (3)	0.0042 (7)	0.6434 (2)	0.47 (8)
O(2)	0.5398 (4)	0.2385 (6)	0.6907 (2)	0.40 (9)
O(3)	0.5026 (4)	0.2518 (6)	0.0841 (2)	0.33 (9)
O(4)	0.7138 (4)	0.2404 (6)	0.7288 (2)	0.42 (9)
O(5)	0.6873 (4)	0.2362 (6)	0.1177 (2)	0.51 (9)
O(6)	0.6439 (4)	0.2459 (6)	0.5102 (2)	0.49 (9)
O(7)	0.3514 (3)	0.0104 (7)	0.3174 (2)	0.50 (9)
O(8)	0.3962 (3)	0.0026 (7)	0.4354 (2)	0.53 (9)
O(9)	0.8589 (4)	0.2454 (7)	0.1527 (2)	0.57 (9)
O(10)	0.8219 (4)	0.2572 (6)	0.5477 (2)	0.44 (9)
O(11)	0.0030 (4)	0.2531 (6)	0.0826 (2)	0.49 (9)
O(12)	0.0384 (3)	-0.0053 (7)	0.3591 (2)	0.37 (8)
O(13)	0.9244 (3)	0.9989 (7)	0.5381 (2)	0.42 (8)
O(14)	0.2482 (4)	0.2423 (7)	0.8363 (2)	0.57 (9)
O(15)	0.2868 (4)	0.2452 (6)	0.9407 (2)	0.54 (9)
O(16)	0.4246 (4)	0.2458 (6)	0.8693 (2)	0.51 (9)
O(17)	0.0695 (4)	0.2611 (7)	0.8009 (2)	0.8 (1)
O(18)	0.1094 (4)	0.2518 (6)	0.4056 (2)	0.41 (9)
O(19)	0.1432 (4)	0.2487 (6)	0.5142 (2)	0.34 (9)
O(20)	0.1764 (4)	0.4874 (7)	0.7887 (2)	0.60 (9)
O(21)	0.7532 (3)	0.9974 (6)	0.5010 (2)	0.40 (8)
O(22)	0.5691 (4)	0.2549 (7)	0.2970 (2)	0.54 (9)
O(23)	0.5289 (3)	0.0112 (7)	0.8593 (2)	0.48 (9)
O(24)	0.6522 (4)	0.4891 (7)	0.6762 (2)	0.9 (1)

Table 2. Geometric parameters ( $\text{\AA}$ )

Mo <sub>7</sub> Cluster I			
Mo(1)—Mo(4)	2.584 (1)	Mo(2)—O(4)	2.137 (6)
Mo(1)—Mo(2)	2.6234 (9)	Mo(3)—O(5)	2.025 (6)
Mo(1)—Mo(3)	2.6652 (9)	Mo(3)—O(8)	2.039 (6)
Mo(1)—Mo(11)	3.1575 (9)*	Mo(3)—O(21)	2.055 (6)
Mo(2)—Mo(6)	2.7165 (9)	Mo(3)—O(10)	2.065 (6)
Mo(2)—Mo(4)	2.735 (1)	Mo(3)—O(6)	2.065 (6)
Mo(2)—Mo(3)	2.7423 (9)	Mo(4)—O(16)	2.005 (6)
Mo(2)—Mo(5)	2.7633 (9)	Mo(4)—O(7)	2.031 (6)
Mo(3)—Mo(5)	2.696 (1)	Mo(4)—O(8)	2.067 (6)
Mo(3)—Mo(7)	2.712 (1)	Mo(4)—O(15)	2.075 (6)
Mo(3)—Mo(4)	2.730 (1)	Mo(4)—O(14)	2.099 (6)
Mo(4)—Mo(6)	2.748 (1)	Mo(5)—O(13)	1.934 (6)
Mo(4)—Mo(7)	2.7798 (9)	Mo(5)—O(10)	1.984 (6)
Mo(5)—Mo(7)	2.700 (1)	Mo(5)—O(12)	2.000 (6)
Mo(5)—Mo(6)	2.729 (1)	Mo(5)—O(9)	2.042 (6)
Mo(6)—Mo(7)	2.6795 (9)	Mo(5)—O(11)	2.137 (6)
Mo(1)—O(5)	2.047 (6)	Mo(6)—O(18)	1.976 (6)
Mo(1)—O(7)	2.056 (6)	Mo(6)—O(20)	1.977 (6)
Mo(1)—O(8)	2.073 (6)	Mo(6)—O(14)	1.985 (6)
Mo(1)—O(2)	2.085 (6)	Mo(6)—O(12)	2.055 (6)
Mo(1)—O(3)	2.110 (6)	Mo(6)—O(17)	2.082 (7)
Mo(1)—O(1)	2.129 (5)	Mo(7)—O(21)	1.922 (6)
Mo(2)—O(5)	2.018 (6)	Mo(7)—O(13)	1.996 (6)
Mo(2)—O(7)	2.024 (6)	Mo(7)—O(15)	2.001 (6)
Mo(2)—O(9)	2.064 (6)	Mo(7)—O(18)	2.031 (6)
Mo(2)—O(20)	2.075 (6)	Mo(7)—O(19)	2.163 (6)
Mo <sub>7</sub> Cluster II			
Mo(8)—Mo(9)	2.610 (1)	Mo(9)—O(14)	2.136 (6)
Mo(8)—Mo(11)	2.632 (1)	Mo(10)—O(26)	2.025 (6)
Mo(8)—Mo(10)	2.676 (1)	Mo(10)—O(2)	2.026 (6)
Mo(8)—Mo(25)	3.171 (1)†	Mo(10)—O(24)	2.038 (6)
Mo(9)—Mo(12)	2.718 (1)	Mo(10)—O(4)	2.065 (6)
Mo(9)—Mo(11)	2.7298 (9)	Mo(10)—O(22)	2.080 (6)
Mo(9)—Mo(10)	2.750 (1)	Mo(11)—O(25)	2.032 (6)
Mo(9)—Mo(13)	2.7630 (9)	Mo(11)—O(2)	2.034 (6)
Mo(10)—Mo(12)	2.720 (1)	Mo(11)—O(26)	2.044 (6)
Mo(10)—Mo(11)	2.751 (1)	Mo(11)—O(31)	2.092 (6)
Mo(10)—Mo(14)	2.786 (1)	Mo(11)—O(1)	2.094 (6)
Mo(11)—Mo(13)	2.717 (1)	Mo(12)—O(30)	1.978 (6)
Mo(11)—Mo(14)	2.728 (1)	Mo(12)—O(27)	1.982 (6)
Mo(12)—Mo(14)	2.7031 (9)	Mo(12)—O(4)	2.000 (6)
Mo(12)—Mo(13)	2.732 (1)	Mo(12)—O(29)	2.019 (6)
Mo(13)—Mo(14)	2.718 (1)	Mo(12)—O(28)	2.081 (6)
Mo(8)—O(26)	2.037 (6)	Mo(13)—O(33)	1.925 (6)
Mo(8)—O(25)	2.041 (6)	Mo(13)—O(31)	1.978 (6)
Mo(8)—O(24)	2.055 (6)	Mo(13)—O(29)	2.028 (6)
Mo(8)—O(16)	2.071 (6)	Mo(13)—O(35)	2.040 (6)
Mo(8)—O(23)	2.093 (6)	Mo(13)—O(32)	2.141 (6)
Mo(8)—O(22)	2.104 (6)	Mo(14)—O(1)	1.956 (6)

Mo(9)—O(25)	2.022 (6)	Mo(14)—O(22)	1.987 (6)	Sr(2)—O(46)	2.886 (6)	Sr(4)—O(1)	2.876 (6)
Mo(9)—O(24)	2.027 (6)	Mo(14)—O(33)	1.999 (6)	Sr(2)—O(30)	2.938 (6)	Sr(4)—O(3)	2.914 (6)
Mo(9)—O(35)	2.055 (6)	Mo(14)—O(30)	2.040 (6)	Sr(2)—O(20)	2.964 (5)	Sr(4)—O(48)	2.945 (6)
Mo(9)—O(27)	2.075 (6)	Mo(14)—O(34)	2.157 (6)	Sr(2)—O(40)	2.984 (6)	Sr(4)—O(8)	3.095 (5)
				Sr(2)—O(23)	3.008 (6)		
<b>Mo<sub>24</sub> Tricuster</b>							
<b>(a) Mo<sub>7</sub> Subcluster</b>							
Mo(15)—Mo(16)	2.616 (1)	Mo(16)—O(36)	2.052 (6)	<b>Ga-atom environments</b>			
Mo(15)—Mo(19)	2.654 (1)	Mo(16)—O(42)	2.055 (6)	Ga(1)—O(35)	1.909 (6)	Ga(2)—O(27)	1.934 (5)
Mo(15)—Mo(17)	2.938 (1)	Mo(16)—O(18)	2.083 (6)	Ga(1)—O(17)	1.936 (6)	Ga(2)—O(37)	1.993 (6)
Mo(16)—Mo(19)	2.670 (1)	Mo(16)—O(41)	2.089 (6)	Ga(1)—O(20)	1.941 (6)	Ga(2)—O(38)	2.058 (6)
Mo(16)—Mo(17)	2.703 (1)	Mo(17)—O(32)	1.984 (6)	Ga(1)—O(37)	1.994 (6)	Ga(2)—O(36)	2.059 (6)
Mo(16)—Mo(20)	2.8045 (9)	Mo(17)—O(11)	1.989 (6)	Ga(1)—O(38)	2.050 (6)	Ga(3)—O(38)	1.830 (5)
Mo(16)—Mo(18)	2.824 (1)	Mo(17)—O(40)	2.092 (6)	Ga(1)—O(40)	2.055 (6)	Ga(3)—O(12)	1.837 (6)
Mo(16)—Mo(18)	3.064 (1)†	Mo(17)—O(36)	2.094 (6)	Ga(2)—O(49)	1.902 (6)	Ga(3)—O(29)	1.851 (5)
Mo(17)—Mo(21)	2.7166 (9)	Mo(17)—O(37)	2.156 (6)	Ga(2)—O(28)	1.912 (6)	Ga(3)—O(37)	1.873 (6)
Mo(17)—Mo(19)	2.720 (9)	Mo(18)—O(19)	2.028 (6)				
Mo(17)—Mo(18)	2.745 (9)	Mo(18)—O(11)	2.041 (6)				
Mo(18)—Mo(20)	2.657 (1)	Mo(18)—O(42)	2.112 (6)				
Mo(18)—Mo(18)	2.780 (1)‡	Mo(18)—O(41)	2.143 (6)				
Mo(18)—Mo(21)	2.788 (1)	Mo(18)—O(41)	2.147 (6)				
Mo(18)—Mo(20)	2.873 (1)‡	Mo(19)—O(43)	2.028 (6)				
Mo(19)—Mo(21)	2.768 (1)	Mo(19)—O(39)	2.028 (6)				
Mo(19)—Mo(20)	2.836 (1)	Mo(19)—O(40)	2.072 (6)				
Mo(19)—Mo(22)	3.0520 (9)§	Mo(19)—O(30)	2.094 (6)				
Mo(20)—Mo(21)	2.681 (1)	Mo(19)—O(46)	2.111 (5)				
Mo(20)—Mo(22)	2.982 (1)§	Mo(20)—O(42)	1.998 (6)				
Mo(21)—Mo(22)	2.7816 (9)§	Mo(20)—O(43)	2.002 (6)				
Mo(21)—Mo(24)	3.0493 (9)§	Mo(20)—O(41)	2.070 (6)				
Mo(21)—Mo(23)	3.059 (1)§	Mo(20)—O(44)	2.084 (5)				
Mo(15)—O(17)	2.019 (6)	Mo(20)—O(10)	2.117 (6)				
Mo(15)—O(28)	2.030 (6)	Mo(21)—O(32)	2.027 (6)				
Mo(15)—O(39)	2.076 (6)	Mo(21)—O(19)	2.043 (6)				
Mo(15)—O(36)	2.078 (6)	Mo(21)—O(45)	2.080 (6)				
Mo(15)—O(40)	2.088 (6)	Mo(21)—O(46)	2.126 (6)				
Mo(15)—O(38)	2.136 (6)	Mo(21)—O(44)	2.135 (6)				
Mo(16)—O(39)	2.023 (6)						
<b>(b) Mo<sub>10</sub> Subcluster</b>							
Mo(22)—Mo(23)	2.7045 (9)	Mo(23)—O(3)	1.944 (6)				
Mo(22)—Mo(25)	2.757 (1)	Mo(23)—O(45)	2.051 (6)				
Mo(22)—Mo(26)	2.7672 (9)	Mo(23)—O(46)	2.104 (5)				
Mo(21)—Mo(24)	2.781 (1)	Mo(23)—O(31)	2.157 (6)				
Mo(23)—Mo(26)	2.7399 (9)	Mo(24)—O(47)	2.026 (6)				
Mo(23)—Mo(25)	2.7423 (9)	Mo(24)—O(48)	2.049 (6)				
Mo(23)—Mo(24)	2.8478 (9)	Mo(24)—O(45)	2.079 (6)				
Mo(24)—Mo(25)	2.5963 (9)	Mo(24)—O(15)	2.083 (6)				
Mo(24)—Mo(26)	2.7072 (9)	Mo(24)—O(44)	2.116 (6)				
Mo(24)—Mo(26)	2.7136 (9)	Mo(25)—O(47)	2.046 (6)				
Mo(25)—Mo(26)	2.7400 (9)	Mo(25)—O(34)	2.054 (6)				
Mo(25)—Mo(26)	2.789 (1)	Mo(25)—O(16)	2.054 (6)				
Mo(26)—Mo(26)	2.838 (1)	Mo(25)—O(23)	2.094 (6)				
Mo(22)—O(34)	2.037 (6)	Mo(25)—O(48)	2.098 (6)				
Mo(22)—O(6)	2.038 (6)	Mo(26)—O(6)	2.028 (6)				
Mo(22)—O(44)	2.114 (6)	Mo(26)—O(47)	2.031 (6)				
Mo(22)—O(46)	2.123 (6)	Mo(26)—O(48)	2.058 (6)				
Mo(22)—O(43)	2.130 (6)	Mo(26)—O(3)	2.060 (6)				
Mo(23)—O(23)	1.930 (6)						
<b>Sr-atom environments</b>							
Sr(1)—O(5)	2.513 (6)	Sr(3)—O(39)	2.640 (6)				
Sr(1)—O(24)	2.566 (6)	Sr(3)—O(21)	2.641 (5)				
Sr(1)—O(47)	2.592 (5)	Sr(3)—O(42)	2.709 (5)				
Sr(1)—O(14)	2.706 (6)	Sr(3)—O(19)	2.732 (6)				
Sr(1)—O(44)	2.759 (6)	Sr(3)—O(13)	2.735 (6)				
Sr(1)—O(15)	2.776 (6)	Sr(3)—O(43)	2.737 (6)				
Sr(1)—O(9)	2.824 (6)	Sr(3)—O(13)	2.923 (5)				
Sr(1)—O(10)	2.834 (6)	Sr(3)—O(11)	2.930 (6)				
Sr(1)—O(41)	2.866 (6)	Sr(3)—O(33)	2.940 (6)				
Sr(1)—O(18)	2.941 (6)	Sr(3)—O(32)	2.955 (6)				
Sr(1)—O(27)	2.955 (6)	Sr(3)—O(29)	3.099 (6)				
Sr(1)—O(36)	3.000 (6)	Sr(3)—O(12)	3.105 (5)				
Sr(2)—O(25)	2.495 (6)	Sr(4)—O(33)	2.557 (5)				
Sr(2)—O(26)	2.548 (6)	Sr(4)—O(21)	2.589 (5)				
Sr(2)—O(7)	2.578 (6)	Sr(4)—O(45)	2.602 (6)				
Sr(2)—O(4)	2.701 (6)	Sr(4)—O(34)	2.658 (6)				
Sr(2)—O(31)	2.776 (6)	Sr(4)—O(48)	2.717 (6)				
Sr(2)—O(22)	2.778 (6)	Sr(4)—O(6)	2.774 (6)				
Sr(2)—O(35)	2.823 (6)	Sr(4)—O(8)	2.795 (6)				

\* Between isolated Mo<sub>7</sub> clusters. † Between isolated Mo<sub>7</sub> clusters and Mo<sub>10</sub> clusters of the tricuster chain fragments. ‡ Between Mo<sub>7</sub> clusters of different tricuster chain fragments within a chain. § Between Mo<sub>7</sub> and Mo<sub>10</sub> subclusters of the same tricuster chain fragment.

Data were corrected for Lorentz and polarization effects. The structure was solved using *SHELXS86* (Sheldrick, 1990) and subsequent difference Fourier syntheses. Refinement of the occupancy factors for the Sr, Ga and Mo sites confirmed that they are fully occupied. Calculations were performed on a Digital Pentium Celebris 590 FP for *SHELXS86* and on a Digital MicroVAX 3100 for the *MolEN* (Fair, 1990) programs.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Lithium Dicobalt Tripolyphosphate and Lithium Dinickel Tripolyphosphate

FATIMA ERRAGH,<sup>a,b</sup> ALI BOUKHARI<sup>a</sup> AND ELIZABETH M. HOLT<sup>c\*</sup>

<sup>a</sup>Laboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V, Avenue Ibn Batouta, Rabat, Morocco, <sup>b</sup>Laboratoire de Chimie Physique de Matériaux, Département de Chimie, Faculté des Sciences, El Jadida, Morocco, and <sup>c</sup>Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@osucc.bitnet

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### Abstract

Isotypic lithium dicobalt triphosphate,  $\text{LiCo}_2\text{P}_3\text{O}_{10}$ , and lithium dinickel triphosphate,  $\text{LiNi}_2\text{P}_3\text{O}_{10}$ , have been synthesized and characterized by single-crystal X-ray diffraction. These are the first observations of non-hydrated mixed-metal tripolyphosphates. The  $\text{P}_3\text{O}_{10}^{5-}$  groups are situated on a mirror plane, with successive  $\text{PO}_3$  moieties displaying both staggered and eclipsed conformations. Octahedrally coordinated  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions form a staggered chain [ $\text{Co} \cdots \text{Co}$  3.286(1) and 3.133(1) Å,  $\text{Ni} \cdots \text{Ni}$  3.201(1) and 3.023(1) Å], with successive metal ions bridged by two O atoms.

### Comment

The literature contains numerous structural studies of solid materials containing the  $\text{P}_3\text{O}_{10}^{5-}$  group. Most, however, are hydrated systems in which hydrogen-bonding

interactions play a role in determining the packing, for example,  $\text{Zn}_5(\text{P}_3\text{O}_{10})_2 \cdot 17\text{H}_2\text{O}$  (Averbuch-Pouchot & Durif, 1975; Averbuch-Pouchot, Durif & Guitel, 1975),  $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$  (Dyroff, 1965),  $\text{CuNa}_3\text{P}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$  (Jouini, Dabbabi, Averbuch-Pouchot, Durif & Guitel, 1984),  $\text{NaZn}_2\text{P}_3\text{O}_{10} \cdot 9\text{H}_2\text{O}$  (powder data; Corbridge & Tromans, 1958) and  $\text{Na}_3\text{NiP}_3\text{O}_{10} \cdot 12\text{H}_2\text{O}$  (powder data; Corbridge & Tromans, 1958). Another group of  $\text{P}_3\text{O}_{10}^{5-}$ -containing complexes reflect their preparation from solution by the inclusion of ammonia in the stoichiometry of the solid, for example,  $(\text{NH}_4)\text{Be}_2\text{P}_3\text{O}_{10}$  (Bagieu-Beucher, Durif & Averbuch-Pouchot, 1976; Averbuch-Pouchot, Durif, Coing-Boyot & Guitel, 1977). A third type of complex is both hydrated and contains  $\text{NH}_4^+$ , for example,  $(\text{NH}_4)_4\text{NaP}_3\text{O}_{10} \cdot 4\text{H}_2\text{O}$  (Averbuch-Pouchot & Durif, 1985). There are few examples of pure ceramics of the type  $M_x\text{P}_3\text{O}_{10}$ . Only  $\text{Ag}_5\text{P}_3\text{O}_{10}$  (ATD data only; Lee, 1968) and two forms of  $\text{Na}_5\text{P}_3\text{O}_{10}$  (Corbridge, 1960; Davies & Corbridge, 1958) are known.

We have prepared the first non-hydrated mixed-metal tripolyphosphates. Lithium dicobalt tripolyphosphate and lithium dinickel tripolyphosphate are isotypic and crystallize with alternating layers of metal atoms and tripolyphosphate groups. The  $\text{P}_3\text{O}_{10}^{5-}$  groups are situated on a mirror plane passing through the P atoms, the bridging O atoms and one O atom of each terminal group. The central P atom of each  $\text{P}_3\text{O}_{10}^{5-}$  group is eclipsed with one neighboring  $\text{PO}_4$  group and shows a staggered arrangement of O atoms with the other neighboring group. P—O—P angles between staggered oxyphosphorus groups are large [143.3(2) and 142.5(3)° for the Co and Ni structures, respectively], but smaller when the adjacent groups are eclipsed [124.8(3) and 126.4(3)° for the Co and Ni structures, respectively] (Fig. 1).

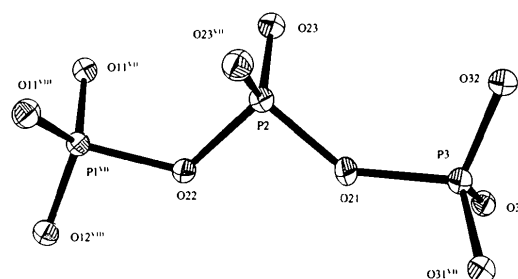


Fig. 1. View of the  $\text{P}_3\text{O}_{10}$  group of lithium dicobalt tripolyphosphate showing the conformation. Displacement ellipsoids are plotted at the 50% probability level.

The transition metal atoms display distorted octahedral coordination geometry with no visible Jahn–Teller distortion for Co [average Co—O 2.136(3) Å and average Ni—O 2.074(3) Å]. The Co and Ni octahedra share edges to form staggered chains. These chains are bridged by edge-sharing octahedral lithium motifs (Fig. 2). The Li atoms are situated on inversion cen-