# A Novel Three-Dimensional Coordination Polymer Involving Pb–Pb Interactions and Three Different Hemidirected Lead(II) Coordination Spheres: X-Ray Crystal Structure of Tris(1,10-phenanthroline-$\kappa N^1$,$\kappa N^{10}$)-bis[{$\mu_3$-[5-(sulfo-$\kappa O$)benzene-1,3-dicarboxylate(3 –)-$\kappa O^1$,$\kappa O^{1'}$:$\kappa O^2$,$\kappa O^{2'}$:$\kappa O^2$]}trilead (*Pb–Pb*) Trihydrate ($[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$)

by **Hong-Ping Xiao**[a]) and **Ali Morsali***[b])

[a]) School of Chemistry and Materials Science, Wenzhou Normal College, Wenzhou 325027,
People's Republic of China

[b]) Department of Chemistry, School of Sciences, Tarbiat Modarres University, P.O. Box 14155-4838,
Tehran, Iran (e-mail: morsali_a@yahoo.com)

---

A novel 3D polymeric Pb$^{II}$ complex involving three different hemidirected Pb$^{II}$ coordination spheres, $[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$ (phen = 1,10-phenanthroline and sip = 5-sulfoisophthalate = 5-sulfobenzene-1,3-dicarboxylate), was synthesized and characterized by elemental analysis and IR spectroscopy. Its single-crystal X-ray structure shows three types of Pb$^{2+}$ ions with coordination number six for Pb(1) and seven for Pb(2) and Pb(3). Two of the lead atoms, Pb(1) and Pb(3), are involved in Pb–Pb interactions.

---

**Introduction.** – The design of crystal structures and control of molecular arrangements of coordination polymers has attracted much attention in recent years [1] [2]. So far, extended systems of a variety of metals have been characterized providing very interesting information about supramolecular isomerism. The Pb$^{II}$ complexes[1]) are interesting and the 'stereochemical activity', *i.e.*, the configurational activity, of valence-shell electron lone pairs is frequently discussed in considering the coordination and configurational activity of heavy metals [4–6].

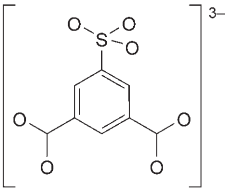
The 5-sulfoisophthalate (= 5-sulfobenzene-1,3-dicarboxylate; sip) anion is an interesting ligand, with both carboxylate and sulfonate groups available as coordinating groups. Because of its ability to form the polynuclear complexes and spontaneous aggregation of several ligand and metal ions, this ligand may also be a very good candidate for the investigation of the configurational activity of valence-shell electron lone pairs in polymeric and supramolecular compounds.

We now report the determination of the structure of a Pb$^{II}$ complex with the ligands 5-sulfoisophthalate (sip) and 1,10-phenanthroline (phen) which provides a novel three-dimensional polymer involving three different hemidirected Pb$^{II}$ coordination spheres and, interestingly, a weak Pb–Pb interaction between two Pb-atoms.

**Results and Discussion.** – Reaction between 'phen' and mixtures of lead(II) acetate trihydrate with 5-sulfoisophthalic acid provided crystalline materials analyzing as

---

[1]) For a review on the coordination chemistry of Pb$^{II}$, see [3].



sip

$[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$. Determination of the solid-state structure of this compound by X-ray crystallography shows that the complex forms a 3D polymeric network containing three types of $Pb^{2+}$ ions with coordination number six for Pb(1) and seven for Pb(2) and Pb(3) (*Figs. 1* and *2*, *Table*). Two of the Pb-atoms, Pb(1) and Pb(3), are involved in weak Pb−Pb interactions (*Fig. 3,a–c*).

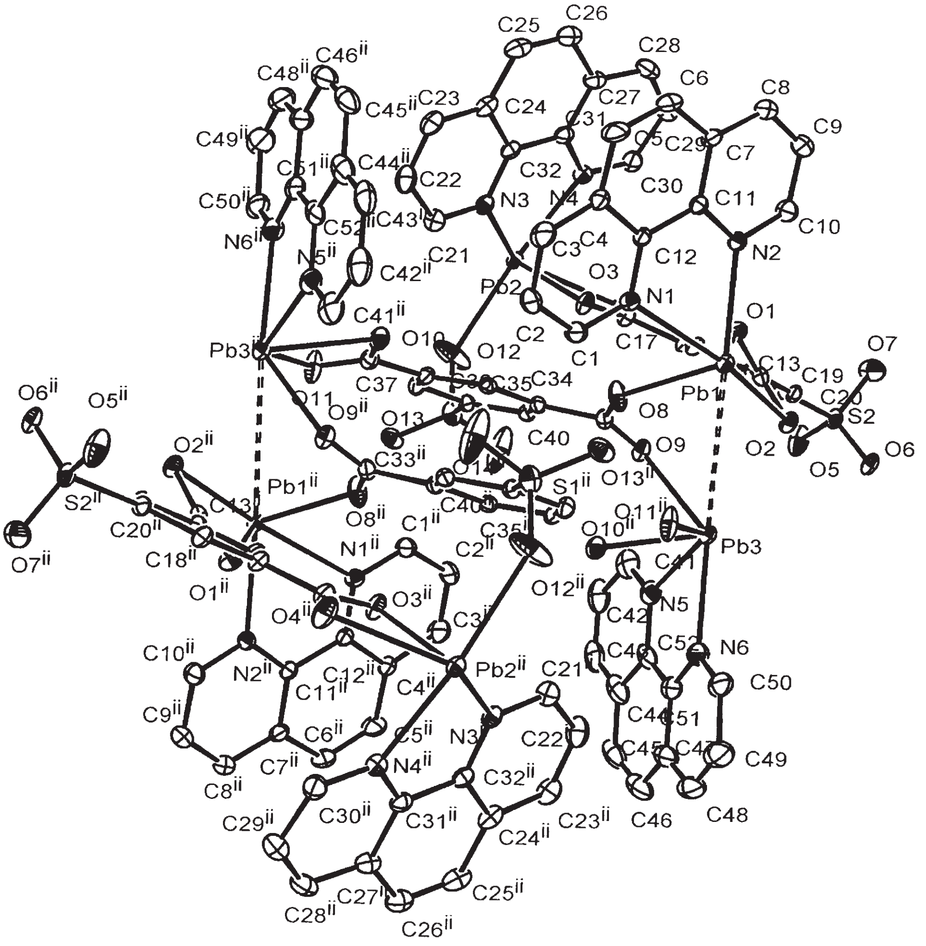


Fig. 1. *X-Ray crystal structure* (ORTEP representation) *of* $[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$. Ellipsoids at 30% probability.

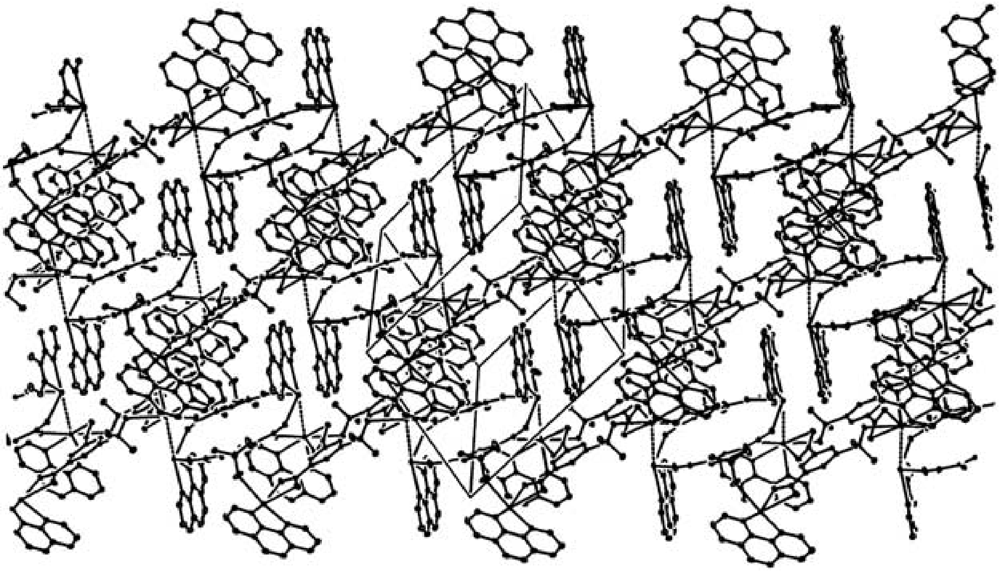


Fig. 2. *Unit cell of* $[\mathrm{Pb_3(phen)_3(H_2O)_2(sip)_2}]_\mathrm{n}\cdot 3\,\mathrm{H_2O}$

Table 1. *Selected Bond Lengths* [Å] *and Angles* [°] *for* $[\mathrm{Pb_3(phen)_3(H_2O)_2(sip)_2}]_\mathrm{n}\cdot 3\,\mathrm{H_2O}$[a]). Arbitrary atom numbering.

| | | | |
|---|---|---|---|
| Pb(1)–O(1) | 2.287(4) | O(1)–Pb(1)–O(8) | 80.51(16) |
| Pb(1)–O(8) | 2.415(4) | O(1)–Pb(1)–N(2) | 76.78(15) |
| Pb(1)–O(2) | 2.996(4) | O(8)–Pb(1)–N(2) | 112.65(17) |
| Pb(1)–O(6)$^{\mathrm{ii}}$ | 2.882(4) | O(1)–Pb(1)–N(1) | 114.37(15) |
| Pb(1)–O(11)$^{\mathrm{ii}}$ | 3.577(4) | O(8)–Pb(1)–N(1) | 70.92(16) |
| Pb(1)–O(7)$^{\mathrm{ii}}$ | 3.481(4) | N(2)–Pb(1)–N(1) | 63.30(14) |
| Pb(1)–N(2) | 2.519(5) | O(3)–Pb(2)–N(4) | 78.04(16) |
| Pb(1)–N(1) | 2.630(5) | O(3)–Pb(2)–N(3) | 79.78(15) |
| Pb(2)–O(3) | 2.369(4) | N(4)–Pb(2)–N(3) | 65.85(16) |
| Pb(2)–O(12) | 2.642(5) | O(3)–Pb(2)–O(12) | 79.87(18) |
| Pb(2)–O(4) | 2.642(4) | N(4)–Pb(2)–O(12) | 151.10(17) |
| Pb(2)–O(13)$^{\mathrm{ii}}$ | 3.034(4) | N(3)–Pb(2)–O(12) | 92.1(2) |
| Pb(2)–O(4W) | 2.889(5) | O(3)–Pb(2)–O(4) | 52.05(14) |
| Pb(2)–N(4) | 2.500(5) | N(4)–Pb(2)–O(4) | 80.07(16) |
| Pb(2)–N(3) | 2.504(5) | N(3)–Pb(2)–O(4) | 126.00(15) |
| Pb(3)–O(10)$^{\mathrm{ii}}$ | 2.442(4) | O(12)–Pb(2)–O4) | 100.6(2) |
| Pb(3)–O(9) | 2.510(4) | O(10)$^{\mathrm{ii}}$–Pb(3)–O(9) | 74.21(14) |
| Pb(3)–N(6) | 2.540(6) | O(10)$^{\mathrm{ii}}$–Pb(3)–N(6) | 76.61(16) |
| Pb(3–O11)$^{\mathrm{ii}}$ | 2.541(5) | O(9)–Pb(3)–N(6) | 137.21(18) |
| Pb(3–O(1W)$^{\mathrm{ii}}$ | 2.970(5) | O(10)$^{\mathrm{ii}}$–Pb(3)–O(11)$^{\mathrm{ii}}$ | 51.94(15) |
| Pb(3)–O(2) | 3.009(4) | O(9)–Pb(3)–O(11)$^{\mathrm{ii}}$ | 99.34(16) |
| Pb(3)–N(5) | 2.545(6) | N(6)–Pb(3)–O(11)$^{\mathrm{ii}}$ | 86.3(2) |
| Pb(1)–Pb(3) | 3.989(6) | O(10)$^{\mathrm{ii}}$–Pb(3)–N(5) | 77.37(16) |
| | | O(9)–Pb(3)–N(5) | 78.68(18) |
| | | N(6)–Pb(3)–N(5) | 126.73(17) |

[a]) Symmetry relation $^{\mathrm{ii}}$ means $-x, -y, -z$.

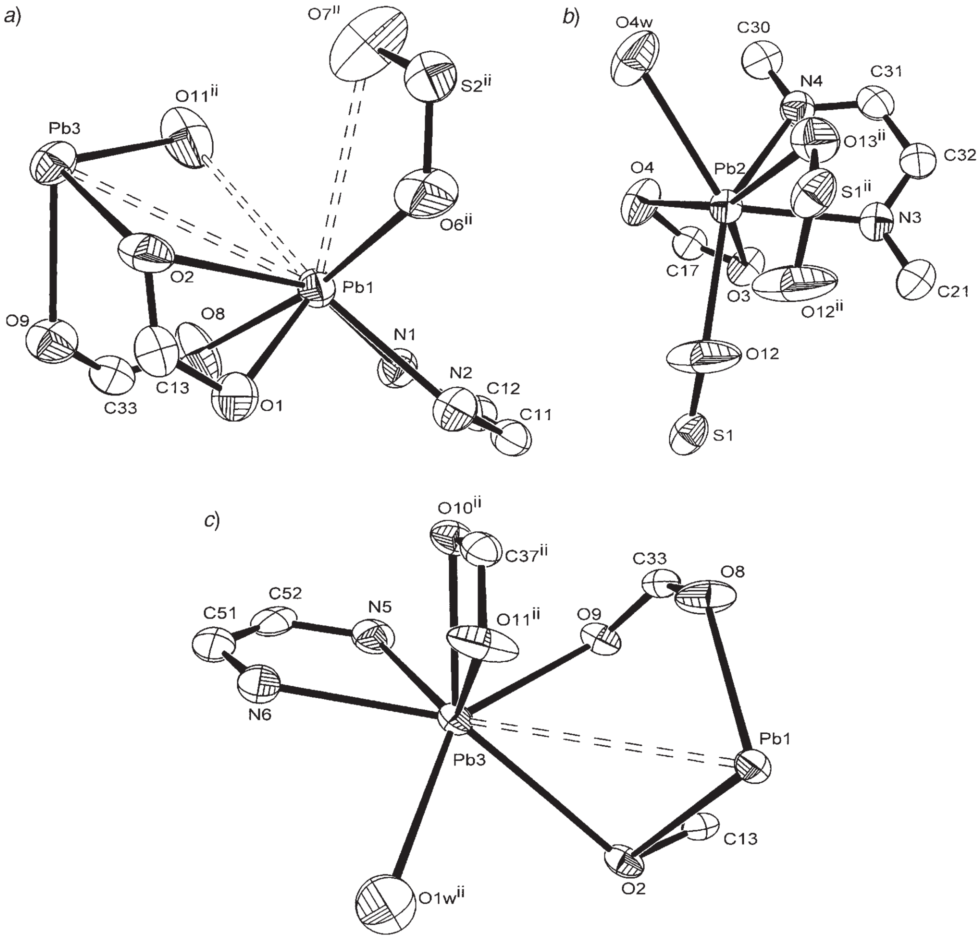


Fig. 3. *Schematic representation of the three different types of* $Pb^{II}$ *environments:* a) *for Pb(1),* b) *for Pb(2), and* c) *for Pb(3)*. Ellipsoids at 30% probability.

Each sip ligand acts as a hexadentate ligand and connects three $Pb^{2+}$ ions. One of the carboxylato groups of sip acts as both bidentate and bridging group (totally tridentate) in a $\mu$-1,3 mode where the two O-atoms coordinate to a $Pb^{2+}$ ion, and one is also involved in a bridge to an adjacent $Pb^{2+}$ ion. The other carboxylato group of sip coordinates only in the bidentate mode, and the sulfato group in the monodentate mode with the remaining two O-atoms being uncoordinated to $Pb^{2+}$ ions (see *Fig. 4*). This coordination mode is quite different from other compounds containing the sip ligand [7][8].

There are three types of $Pb^{II}$ ions: a $Pb(1)N_2O_4$ moiety with coordination number six, and a $Pb(2)N_2O_5$ and a $Pb(3)N_2O_5$ moiety with a coordination number seven each. There is also a weak interaction of Pb(1) with the O-atom $O(11)^{ii}$ and $O(7)^{ii}$ of the sip ligands ($Pb(1)-O(11)^{ii}$ 3.577 Å and $Pb(1)-O(7)^{ii}$ 3.481 Å; see the *Table*). In fact, each Pb-atom in this structure, besides six normal bonds, forms two 'weak' Pb···O bonds,

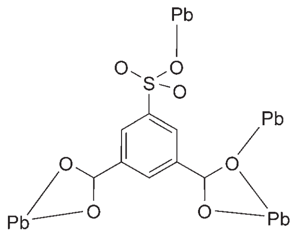


Fig. 4. *Coordination modes of the carboxylato and sulfato groups in the complex* $[Pb_3(phen)_3(H_2O)(sip)_2]_n \cdot 3\,H_2O$

thus the coordination number for the Pb-atoms can be considered to be eight ($PbN_2O_6$) (see *Fig. 1* and *Fig. 3,a*). The presence of a lone pair of the Pb-atom is apparently the reason that the bridging interactions cannot come closer together. The absence of a configurationally active lone pair would create more bridging interactions between the $Pb^{II}$ atoms and the neighboring O-atoms of the sip ligands, and hence would lead to more symmetry.

There is an other new interaction between the Pb(1) and Pb(3) atoms. The extent of direct Pb–Pb interactions has been rarely reported. Some Pb–Pb interactions between 'adjacent' Pb-atoms with distances 3.44–4.09 Å in the clusters have been reported [9][10]. The separation between the two Pb-atoms in $[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$ is 3.989(6) Å, which is smaller than the sum [10] of *van der Waals* radii of two $Pb^{II}$ atoms, hence, suggesting a weak metallophilic Pb–Pb interaction. Therefore, the Pb(1) and Pb(3) centers can be nine- and eight-coordinate, respectively, with coordination to two N-atoms of one phen ligand, to six and and five O-atoms, respectively, of the sip ligands, and to one $Pb^{II}$ atom, resulting in the environment around Pb(1) and Pb(3) as $N_2O_6Pb(1)-Pb(3)N_2O_5$.

The arrangement of the phen and sip ligands suggests a gap or hole in the coordination geometry around the three $Pb^{2+}$ ions (the angles $O(6)^{ii}-Pb(1)-N(1)$, $O(4W)-Pb(2)-O(12)$, and $O(13)^{ii}-Pb(3)-O(4)$ are 125.04(2), 100.6(2), and 157.10(8)° around Pb(1), Pb(2), and Pb(3), resp.), occupied possibly by a configurationally active lone pair of electrons on the $Pb^{II}$ atoms. The geometry of the nearest coordination environment around every Pb atom is probably also caused by the geometrical constraints of the ligands phen and sip besides the influence of a configurationally active lone pair of electrons in a hybrid orbital on the metal atoms. Hence, the geometry with respect to Pb(1), Pb(2), and Pb(3) is hemidirected (see *Fig. 3,a–c*) [6].

There is a noticeable lack of solvent bound to $Pb^{II}$ [6], and the $H_2O$ coordinated $Pb^{II}$ compounds are rare. This is in line with the low solubility of lead compounds in general. The $[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$ complex contains two $H_2O$ molecules coordinated to the Pb(1) and Pb(2) centers. There are three $H_2O$ molecules that are not coordinated to the Pb-atoms.

Also both edge-to-face and edge-to-edge $\pi-\pi$ stacking [11][12] interactions between aromatic rings belonging to adjacent chains are present in the network of the studied complex, as shown in *Fig. 5*. There are edge-to-face $\pi-\pi$ stacking interactions between the phen and sip ligands with the distance 3.63 Å (*Fig. 5,a*). There are also

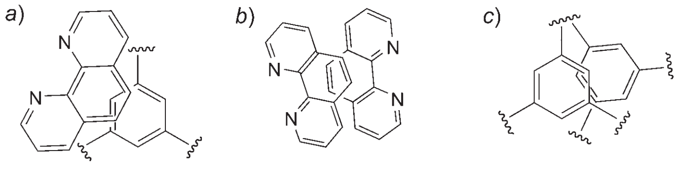


Fig. 5. *Projection of nearest-neighbor pairs in the $\pi-\pi$ stacks of aromatic rings in $[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$*

edge-to-edge $\pi-\pi$ stacking interactions between two phen ligands (*Fig. 5,b*) and between two sip ligands (*Fig. 5,c*) with the distances 3.72 and 3.56 Å, respectively.

The structure of $[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$ is interesting because it represents a new, rarely observed three-dimensional framework with three different hemidirected $Pb^{II}$ coordination spheres, and because it is a new complex involving weak Pb−Pb interactions.

The authors acknowledge financial support by the *Zhejiang Provincial Natural Science Foundation* (No. Y404294), the *Wenzhou Science and Technology Project of China* (No. S2003A008), the *'551' Distinguished Person Foundation of Wenzhou*, and the Tarbiat Modarres University of Iran.

## Experimental Part

*Tris(1,10-phenanthroline-κ*$N^1$*,κ*$N^{10}$*)bis{μ*$_3$*-[5-(sulfo-κO)benzene-1,3-dicarboxylato(3−)-κ*$O^1$*,κ*$O^{1'}$*:κ*$O^2$*,-κ*$O^{2'}$*:κ*$O^2$*]}trilead(Pb−Pb) Trihydrate (*$[Pb_3(phen)_3(H_2O)_2(sip)_2]_n \cdot 3\,H_2O$*).* Lead(II) acetate trihydrate (0.5 mmol), 5-sulfoisophthalic acid (0.5 mmol), and 1,10-phenanthroline (1.0 mmol) were placed in a 30-ml, *Teflon*-lined, stainless-steel *Parr* bomb together with $H_2O$ (18 ml). The bomb was heated at 423 K for three days and then cooled slowly to r.t. to furnish colorless crystals. IR (selected signals; $cm^{-1}$): 3419*s*, 3083*w*, 1607*vs*, 1546*s*, 1421*s*, 1348*s*, 1175*s*, 1093*m*, 1027*m*, 849*s*, 774*m*, 718*m*, 618*m*. Anal. calc. for $C_{104}H_{70}N_{12}O_{37}Pb_6S_4$: C 36.16, H 2.03, N 4.86; found: C 36.10, H 1.98, N 4.91.

*X-Ray Crystal Structure.* A single crystal of dimensions 0.38 × 0.14 × 0.12 mm was analyzed at 273(2) K with a *Bruker APEX* area-detector diffractometer. The intensity data were collected within the range $1.40° \leq \theta \leq 28.27°$ by using graphite monochromated Mo$K_\alpha$ radiation ($\lambda$ 0.71073 Å). Accurate unit-cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The intensities of 10753 unique reflections were collected, of which 9117 were considered observed by the criterion $I > 2\sigma(I)$ (SHELXS-97) [13]. The structure was solved by direct methods and refined by full-matrix least-squares techniques on $F^2$ (SHELXL-97) [14]. The positions of the H-atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each H-atom was assigned an isotropic thermal parameter. Crystal data: $C_{104}H_{70}N_{12}O_{37}Pb_6S_4$, $M_r$ 3451.10; triclinic, space group $P\bar{1}$; $a = 12.9865(7)$, $b = 14.8094(9)$, $c = 15.4210(9)$ Å, $\alpha = 85.1470(10)$, $\beta = 71.6120(10)$, $\gamma = 79.5440(10)°$, $V = 2766.5(3)$ Å$^3$, $Z = 1$, $D_c = 2.071$ Mg/m$^3$; $F(000) = 1630$, $R(wR) = 0.0344$ (0.0889) for 10190 reflections with $I > 2\sigma(I)$.

CCDC-267291 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

## REFERENCES

[1] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629.
[2] D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375.
[3] J. Parr, *Polyhedron* **1997**, *16*, 551.
[4] P. Pyykkö, *Chem. Rev.* **1988**, *88*, 563.
[5] J. M. Harrowfield, H. Miyamae, B. W. Skelton, A. A. Soudi, A. H. White, *Aust. J. Chem.* **1996**, *49*, 1165 and refs. cit. therein.
[6] L. Shimoni-Livny, J. P. Glusker, C. W. Brock, *Inorg. Chem.* **1998**, *37*, 1853.

[7] J. Tao, X. Yin, R.-B. Huang, L.-S. Zheng, S. W. Ng, *Acta Crystallogr.*, *Sect. E* **2003**, *59*, m611.
[8] X.-H. Li, H.-P. Xiao, Q. Zhang, M.-L. Hu, *Acta Crystallogr.*, *Sect. C* **2005**, *61*, m130.
[9] T. G. Spiro, D. H. Templeton, A. Zalkin, *Inorg. Chem.* **1969**, *8*, 856.
[10] C. Gaffney, P. G. Harrison, T. J. King, *J. Chem. Soc.*, *Chem. Commun.* **1980**, 1251.
[11] I. G. Dance, M. L. Scudder, *J. Chem. Soc.*, *Dalton Trans.* **1996**, 3755.
[12] Z.-H. Liu, C.-Y. Duan, J.-H. Li, Y.-J. Liu, Y.-H. Mei, X.-Z. You, *New J. Chem.* **2000**, *24*, 1057.
[13] G. M. Sheldrick, 'SHELXS 97, Program for Crystal Structure Solution', University of Göttingen, 1997.
[14] G. M. Sheldrick, 'SHELXL 97, Program for Crystal Structure Refinement', University of Göttingen, 1997.

*Received April 14, 2005*