Available online at www.sciencedirect.com

ScienceDirect

Inorganic Chemistry Communications 10 (2007) 1189–1193

INORGANIC CHEMISTRY COMMUNICATIONS

www.elsevier.com/locate/inoche

A novel tetranuclear cubic cage, $[Tl_4(\mu_3\text{-dcp})_4]$ {Hdcp=2,4-dichlorophenol, new short Cl···Cl interactions, thermal, fluorescence, structural and solution studies

Kamran Akhbari, Ali Morsali *

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Islamic Republic of Iran

Received 9 May 2007; accepted 18 June 2007
Available online 29 June 2007

Abstract

The single crystal X-ray analysis of a novel Tl^I complex of 2,4-dichlorophenol (Hdcp) ligand shows that the complex has a tetranuclear cubic cage as a result of bridging ligands dcp^- with basic repeating of $[Tl(\mu_3\text{-dcp})]$ units. There are four thallium atoms with similar coordination spheres in the cubic cage. These thallium atoms contain irregular coordination sphere with stereo-chemically active lone pair. The thermal stability of $[Tl_4(\mu_3\text{-dcp})_4]$ was studied by thermal gravimetric (TG) and differential thermal analyses (DTA). The compound $[Tl_4(\mu_3\text{-dcp})_4]$ is luminescent in the solution state with emission maxima at 397 nm. The results of studies of the stoichiometry and formation of $[Tl_4(\mu_3\text{-dcp})_4]$ complex in DMF solution were found to be in support of their solid state stoichiometry.

Keywords: 2,4-Dichlorophenol; Thallium; Tetranuclear cage

The Tl^I compounds are interesting and frequently discussed in considering the "stereo-chemical activity" of valence shell electron lone pairs, potential ability to form metal–metal bonds and also complexes with aromatic hydrocarbons [1–27]. The Tl ion is nonspherical, with its inert pair ($6s^2$) partially hybridized leading to the formation of a local dipole that may strongly affect cation···ligand interactions. This "inert-pair effect" has, in a general way, been explained by Pitzer [28] and by Pykkö and Desclaux [29] as a relativistic effect causing the outers electrons to be more strongly attracted to the nucleus than normally expected. In p-block cations with an $ns^2\ np^0$ electronic configuration, lone pairs of electrons may thus play a prominent role in controlling the structures and chemical behavior. In inorganic salts, the lone pair is manifested by a distortion of regular coordination geometries by a substantial elongation of certain bonds, as exemplified in, for example, TlF [30], $Tl[CuAsO_4]$, $Tl[CuPO_4]$ [31] or $TlZn(PO_3)_3$ [32]. In several organometallic compounds, the stereo-active lone pair is manifested by a "half-naked" cation, with ligands only coordinating one hemisphere, as observed in the crystal structures of complexes between Tl(I) and tris(pyrazolyl)borate, where the lone pair occupies the fourth position of a tetrahedron bis(pyrazolyl)phosphinate [33], with an obvious gap in the coordination sphere due to the lone pair, and also in $[Tl_2(\mu\text{-Htdp})_2(\mu\text{-}H_2O)]_n$ ($H_2tdp = 4,4$-thiodiphenol) [34]. Although, in most of thallium compounds the lone pair is stereo-chemically active [35] but there are several compounds in which the lone pair is inactive [36,37]. In this work we wish to examine the structural characteristics of the novel Tl(I) complex with the ligand 2,4-dichlorophenol (Hdcp), in addition thermal, emission and solution studies of this compound were done. Complexes of this ligand are very sparse and our search shows that compound $[Tl_4(\mu_3\text{-dcp})_4]$ is the first complex of this ligand with short and very interesting Cl···Cl interactions that make this compound as a coordination polymer.

---

* Corresponding author. Tel.: +98 218011001; fax: +98 218009730.
E-mail address: morsali_a@yahoo.com (A. Morsali).

1387-7003/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2007.06.017

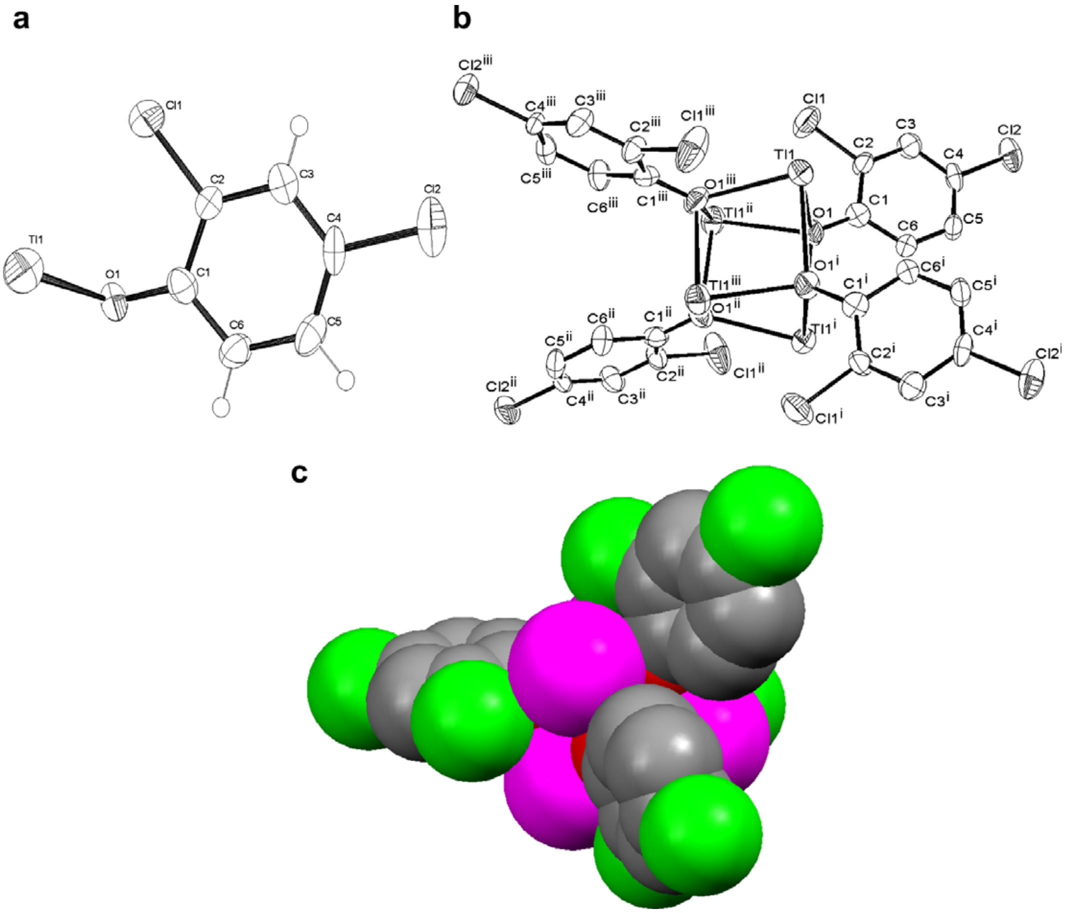
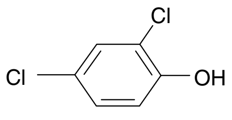


Fig. 1. (a) ORTEP diagram, (b) view of the Tl environment; showing the tetranuclear cubic cage, (c) Space-filling representations of compound $[Tl_4(\mu_3\text{-}dcp)_4]$. (Tl = purple, O = red, C = gray, Cl = green). i: $-x$, $-y+1/2$, $z+1/2$; ii: $x+1/4$, $-y+1/4$, $-z+1/4$; iii: $-x+1/4$, $y+3/4$, $-z+1/4$.



Hdcp

The reaction between 2,4-dichlorophenolate (dcp^-) and $Tl^I(NO_3)$ provided crystalline materials of the general formula $[Tl_4(\mu_3\text{-}dcp)_4]$ [48]. Determination of the structure of this compound by X-ray crystallography (Table S1 and S2) showed the compound has a novel tetranuclear cubic cage (Figs. 1 and 2)[1] with four Tl^+-ions and with coordination numbers of three. Tl atoms are coordinated with three phenolic oxygen atoms with Tl–O distances of *ca.* 2.50–2.75 Å. The phenolic oxygen atom of the "dcp^-" ligand acts as bridging group (totally with three bonding interactions) (Scheme 1).

There are interactions between the Tl1 and two other thallium atoms in the cage. The distances between them are 3.845(2) Å, smaller than the sum of van der Waals radii of two Tl(I) [9]. The distances between the other thallium atoms within the cage are 4.393(2), longer than the sum [38] of van der Waals radii of two Tl^I. Hence, two metallophilic Tl···Tl interactions for Tl1 atoms in compound $[Tl_4(\mu_3\text{-}dcp)_4]$ may be considered. However, the Tl-ions in this compound may be considered five-coordinate, the resulting environment being as TlO_3Tl_2. In $[Tl_4(\mu_3\text{-}dcp)_4]$, the lone pair of Tl(I) atoms is "active" in the solid state. Indeed, the arrangement of O atoms suggests a gap or hole in coordination geometry around the Tl(I) coordination sphere (Fig. 1), a gap possibly occupied by a "stereo-active" electron lone pair. Hence, the geometry of the nearest coordination environment of every Tl(I) atoms is likely to be caused by the geometrical constraints of coordinated O and Tl atoms and by the influence of a stereo-chemically "active" electron lone pair on the metal. Four thallium atoms and four oxygen atoms of dcp^- anions form a new interesting cage with distorted cubic geometry (Fig. 1). These tetranuclear cubic cages act as nodes and are connected through Cl···Cl interactions to four other nodes (Fig. 3), resulting in a two-dimensional network as shown in Fig. 2. However, the other interesting feature of this complex is that, there is the shortest Cl···Cl interactions (Fig. 2) with the distances of Cl3···Cl3 $[2-x, 2-y, 1-z] = 3.233(2)$ Å that is less than the sum of the van

---

[1] For interpretation of colours in Figs. 1 and 2, the reader is referred to the web version of this article.

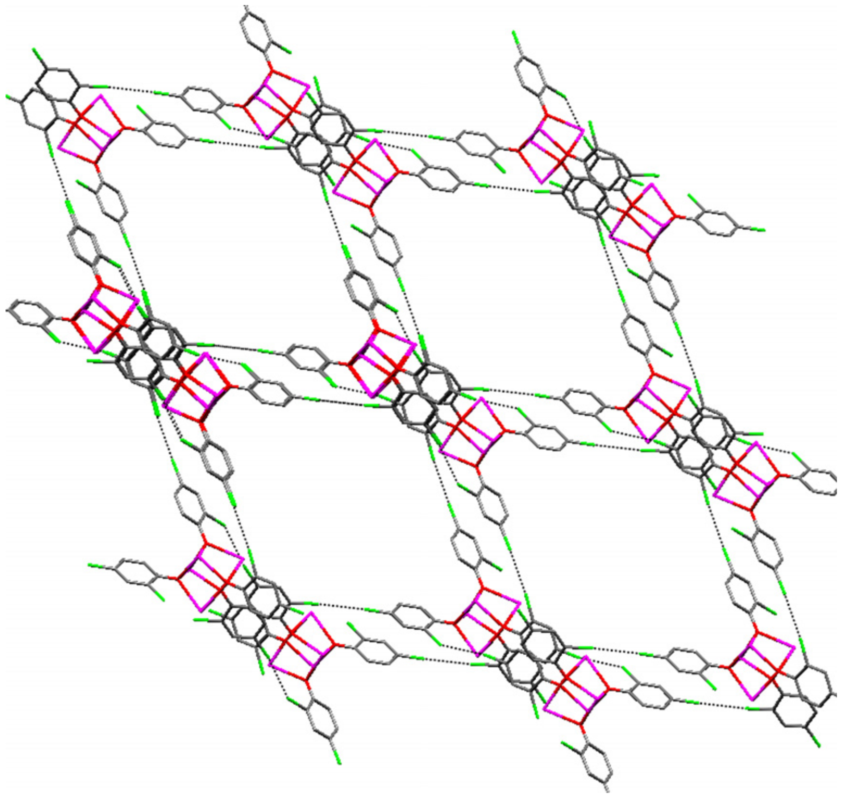
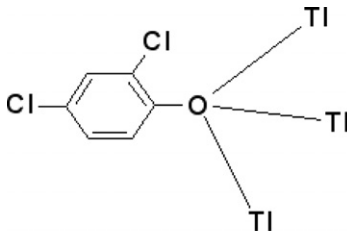


Fig. 2. A fragment of the two-dimensional layer in compound $[Tl_4(\mu_3\text{-dcp})_4]$, showing the Cl···Cl interactions. H atoms are omitted for clarity.



Scheme 1.

der Waals radii of two Cl atoms that is 3.6 Å [39]. Indeed, it is now realized that Cl···Cl interactions can also play a significant and predictable structure-determining role in the chlorine-substituted phenolic metal ion complexes. Hence, interhalogen interactions are capable of affecting the realized crystalline architecture of solid organic compounds decisively, and they may thus be used as tools in crystal engineering [40–46]. It has been shown that the Cl···Cl interactions can be indicative of hypervalent (n–σ^*) Cl–Cl contacts [47].

To examine the thermal stability of compound $[Tl_4(\mu_3\text{-dcp})_4]$, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700 °C in the static atmosphere of air. Compound $[Tl_4(\mu_3\text{-dcp})_4]$ melts at 183 °C. TG curve exhibits a loss of weight between 183 and 376 °C with a mass loss of 19.9% (calcd 19.3%). Because of formation of a weak bond between C–Cl, this stage could be related to remove of Cl_2 from this compound. The next loss of weight correlated to decomposition of the end residue. DTA curve displays two distinct exothermic peaks at 316 and 573 °C and two endothermic peaks at 183 and 426 °C (Fig. S1).

The fluorescence spectra of compound $[Tl_4(\mu_3\text{-dcp})_4]$ has been studied in DMF solution. The compound shows a broad emission band with the maximum intensity at 397 nm upon excitation at 300 nm, (Fig. 3). This fluorescent emission can be tentatively assigned to MMCT and the existence of thallium–thallium interactions in the solu-

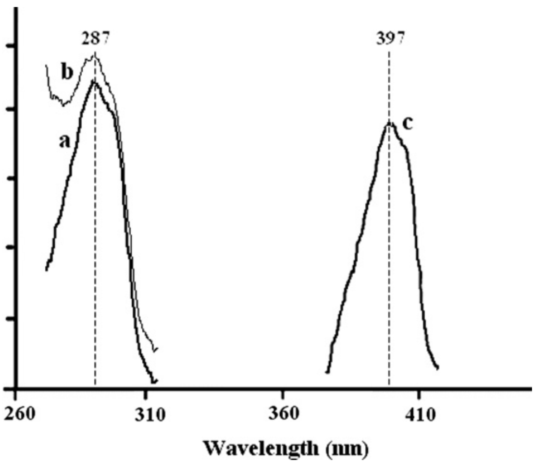


Fig. 3. Electronic absorption of ligand Hdcp (a) Electronic absorption of compound $[Tl_4(\mu_3\text{-dcp})_4]$. (b) Absorption: $c = 1.36 \times 10^{-4}$ mol l^{-1}, DMF, $d = 1$ cm for both ligand Hdcp and compound $[Tl_4(\mu_3\text{-dcp})_4]$. The fluorescence spectra of $[Tl_4(\mu_3\text{-dcp})_4]$ in DMF solution. Room temperature, $\lambda_{exc} = 300$ nm.

tion state as there is not any similar emission for the free ligand Hdcp upon the same excitation at 300 nm (Fig. 3), the luminescent behavior observed for this complex also indicates that the structure of this complex is kept in solution state [49–51].

The electronic absorption spectra of the ligand dcp$^-$ in the presence of increasing concentration of thallium(I) ion in DMF at room temperature are shown in Fig. S2. As is obvious, the strong absorption of ligand at 287 nm increases with increasing concentration of the metal ion. The resulting absorbance (at 287 nm) against [Tl$^+$]/[dcp$^-$] mole ratio plot, shown in the inset of Fig. S2, revealed a distinct inflection point at metal-to-ligand molar ratio of about 1, emphasizing the formation of a 1:1 complex in solution. The formation and stoichiometry of the Tl$^+$-dcp$^-$ complex in DMF solution were also investigated by a conductometric method. The conductivity of a 5.0×10^{-5} M solution of thallium(I) nitrate solution in DMF was monitored as a function of [dcp$^-$]/[Tl$^+$] mole ratio at 25.00 ± 0.05 °C and the resulting plot is shown in Fig. S3. As it is seen, the initial conductivity is relatively low, probably due to some degree of ion pairing which is common in solvents with relatively low dielectric constant like DMF. Addition of the ligand to the metal salt solution then do not causes a variation in the solution conductivity possessing a rather distinct inflection point at a molar ratio of about 1, indicating the formation of a 1:1 Tl$^+$-dcp$^-$ complex in solution.

For evaluation of the conditional formation constants, the mole ratio data obtained by the two different physicochemical methods employed were fitted to the previously reported equations [52,53] using a non-linear least-squares curve fitting program KINFIT [54]. The conditional formation constants of the complex were evaluated as 2.58 ± 0.003 and 2.47 ± 0.1 from the spectrophotometric and conductometric methods, respectively.

In summary, a novel Tl^{I} tetranuclear cubic cage of 2,4-dichlorophenol (Hdcp) ligand, [Tl$_4$(μ_3-dcp)$_4$], was synthesized and characterized. These thallium atoms contain irregular coordination sphere with stereo-chemically active lone pair. The results of studies of the stoichiometry and formation of [Tl$_4$(μ_3-dcp)$_4$] in DMF solution were found to be in support of their solid state stoichiometry. This compound has shown luminescent properties in DMF solution.

Acknowledgement

Support of this investigation by Iran National Science Foundation, INSF (Project Number 84118) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 643425 contains the supplementary crystallographic data for [Tl$_4$(μ_3-dcp)$_4$]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.06.017.

References

[1] H.M. Alvarez, P.A. Gillespie, C.D. Gause, Polyhedron 23 (2004) 617.
[2] R.P. Sharma, R. Bala, J. Mol. Struct. 249 (2005) 738.
[3] P. Pyykk, M. Straka, T. Tamm, Phys. Chem. Chem. Phys. 1 (1999) 3441.
[4] H. Schumann, C. Janiak, J. Pickardt, U. Borner, Angew. Chem., Int. Ed. 26 (1987) 789.
[5] C. Janiak, R. Hofmann, J. Am. Chem. Soc. 112 (1990) 5924.
[6] P.H.M. Budzelaar, J. Boersma, Recl. Trav. Chim. Pays-Bas 109 (1990) 187.
[7] H. Schumann, C. Janiak, M.A. Khan, J.J. Zuckerman, J. Organomet. Chem. 354 (1988) 7.
[8] H. Schmidbaur, W. Bublak, J. Riede, G. Muller, Angew. Chem., Int. Ed. 24 (1985) 414.
[9] W. Frank, G. Korrell, G.J. Reiß, J. Organomet. Chem. 506 (1996) 293.
[10] S. Strauss, H.M.D. Noirot, O.P. Anderson, Inorg. Chem. 25 (1986) 3850.
[11] M.D. Noirot, O.P. Anderson, S.H. Strauss, Inorg. Chem. 26 (1987) 2216.
[12] M.A. Bandman, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 27 (1988) 2399.
[13] H. Schmidbaur, W. Bublak, B. Huber, J. Hofmann, G. Muller, Chem. Ber. 122 (1989) 265.
[14] J. Beck, J. Strahle, Z. Naturforsch. 41b (1986) 1381.
[15] S.D. Waezsada, T. Belgardt, M. Noltemeyer, H.W. Roesky, Angew. Chem., Int. Ed. 33 (1994) 1351.
[16] P. Ghosh, A.L. Rheingold, G. Parkin, Inorg. Chem. 38 (1999) 5464.
[17] T. Fillebeen, T. Hascall, G. Parkin, Inorg. Chem. 36 (1997) 3787.
[18] M.D. Noirot, O.p. Anderson, S.H. Strauss, Inorg. Chem. 26 (1987) 2216.
[19] A. Askarinejad, Ali Morsali, Helv. Chim. Acta 89 (2006) 265.
[20] A. Askarinejad, Ali Morsali, Inorg. Chem. Commun. 9 (2006) 143.
[21] A. Askarinejad, A. Morsali, J. Org. Chem. 691 (2006) 3563.
[22] A. Askarinejad, A. Morsali, Inorg. Chim. Acta 359 (2006) 3379.
[23] A. Askarinejad, A. Morsali, L.-G. Zhu, Solid State Sci. 8 (2006) 537.
[24] E. Craven, D. Mutlu, S. Lundberg, S. Temizdemir, H. Dechert, C. Brombacher, C. Janiak, Polyhedron 21 (2002) 553.
[25] C. Janiak, Coord. Chem. Rev. 163 (1997) 107.
[26] A.-V. Mudring, F. Rieger, Inorg. Chem. 44 (2005) 6240.
[27] M.V. Childress, D. Millar, T.M. Alam, K.A. Kreisel, G.P.A. Yap, L.N. Zakharov, J.A. Golen, A.L. Rheingold, L.H. Doerrer, Inorg. Chem. 45 (2006) 3864.
[28] K.S. Pitzer, Acc. Chem. Res. 12 (1979) 271.
[29] P. Pyykkö, J.P. Desclaux, Acc. Chem. Res. 12 (1979) 276.
[30] N.W. Alcock, H.D.B. Jenkins, J. Chem. Soc., Dalton Trans. (1974) 1907.
[31] P. Moser, H.M. Schwunck, W. Jung, Z. Anorg. Allg. Chem. 624 (1998) 1256.
[32] A. El Abiad, B. Es-Sakhi, M. Mesnaoui, M. Maazaz, I. Belharouak, P. Graveraeau, C. Parant, G. Wallez, G. Le Flem, J. Solid State Chem. 154 (2000) 584.
[33] (a) P.L. Jones, K.L.V. Mann, J.C. Jerrery, J.A. McCleverty, M.D. Ward, Polyhedron 16 (1997) 2435;
(b) D.A. Bardwell, J.C. Jerrery, J.A. McCleverty, M.D. Ward, Inorg. Chim. Acta 267 (1998) 232.

[34] K. Akhbari, Ali. Morsali, A.D. Hunter, M. Zeller, Inorg. Chem. Commun. 10 (2007) 178.

[35] S.-H. Huang, R.-J. Wang, T.C.W. Mak, J. Chem. Soc., Dalton Trans. (1991) 1379.

[36] E.J. Fernandez, A. Laguna, J.M. Lopez-de-Luzuriaga, M. Monge, M. Montiel, M.E. Olmos, Inorg. Chem. 46 (2007) 2953.

[37] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M.E. Olmos, J. Pérez, Chem. Commun. (2003) 1760.

[38] F. Wiesbrock, H. Schmidbaur, J. Am. Chem. Soc. 125 (2003) 3622.

[39] H. Zhu, Z. Chu, D. Hu, W. Huang, S. Gou, Inorg. Chem. Commun. 10 (2007) 362.

[40] J.A.R.P. Sarma, G.R. Desiraju, Acc. Chem. Res. 19 (1986) 222.

[41] G.R. Desiraju, Crystal Engineering: The Design of Organic Solids, Materials Science Monographs, vol. 54, Elsevier, Amsterdam, 1989.

[42] G.R. Desiraju, Angew. Chem., Int. Ed. Engl. 107 (1995) 2541.

[43] G.R. Desiraju, in: D.D. MacNicol, F. Toda, R. Bishop (Eds.), Comprehensive Supramolecular Chemistry, vol. 6, Elsevier, Oxford, 1996, p. 1.

[44] G.R. Desiraju, J. Chem. Soc. Chem. Commun. (1997) 1475.

[45] A. Anthony, G.R. Desiraju, R.K.R. Jetti, S.S. Kuduva, N.N.L. Madhavi, A. Nangia, R. Thaimattan, V.R. Thalladi, Cryst. Eng. 1 (1998) 1.

[46] E. Weber (Ed.), Design of Organic Solids, Topics in Current Chemistry, vol. 198, Springer-Verlag, Berlin, Heidelberg, 1998.

[47] S. Herres-Pawlis, U. Florke, G. Henkel, Inorg. Chem. Commun. 9 (2006) 996.

[48] 1 mmol (0.163 g) of 2,4-Dichlorophenol was dissolved in 20 ml acetonitril and was mixed and refluxed with solution of 1 mmol (0.057 g) KOH in 3 ml H_2O, then a solution of 1 mmol (0.266 g) $TlNO_3$ in 5 ml H_2O was added to the mixture and was refluxed for 2 h. After filtering it was allowed to evaporate for several days and then suitable colourless crystals were obtained. The crystals were washed with acetone and air dried, m.p. = 183 °C, Yield: 0.161 g (44%). IR (selected bands; in cm^{-1}): 540 m, 606 m, 640 s, 715 vs, 809 s, 845 m, 1034 m, 1083 m, 1274 s, 1302 s, 1386 m, 1454 vs and 1563 m. Anal. calc. for $C_6H_3Cl_2OTl$: C, 19.65; H, 0.81; Tl, 55.68%; found; C, 19.80; H, 1.00.

[49] E.J. Fernandez, J.M. Lopez-de-Luzuriaga, M. Elena Olmos, J. Perez, Inorg. Chem. 44 (2005) 6012.

[50] E.J. Fernandez, J.M. Lopez-de-Luzuriaga, M. Monge, M.E. Olmos, J. Perez, J. Am. Chem. Soc. 124 (2002) 5942.

[51] E.J. Fernandez, A. Laguna, J.M. Lopez-de-Luzuriaga, M. Montiel, M.E. Olmos, J. Perez, Inorg. Chim. Acta. 358 (2005) 4293.

[52] M.R. Ganjali, A. Rouhollahi, A.R. Mardan, M. Shamsipur, J. Chem. Soc., Faraday Trans. 94 (1998) 1959.

[53] A. Fakhari, M. Shamsipur, J. Incl. Phenom. 26 (1996) 243.

[54] V.A. Nicely, J.L. Dye, J. Chem. Educ. 49 (1971) 443.