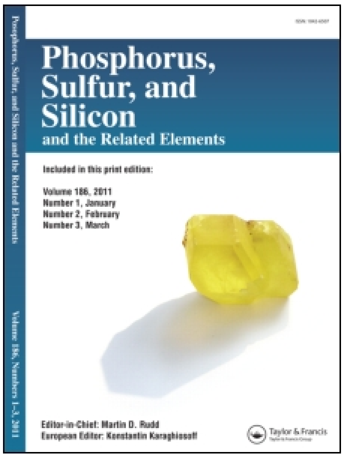

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

RECENT DEVELOPMENTS ON THE STRUCTURAL CHEMISTRY OF COMPLEXES OF SELENIUM AND TELLURIUM WITH SULFUR-AND SELENIUM CONTAINING LIGANDS

Steinar Husebye[a]
[a] Department of Chemistry, University of Bergen, Bergen, Norway

To cite this Article Husebye, Steinar(1988) 'RECENT DEVELOPMENTS ON THE STRUCTURAL CHEMISTRY OF COMPLEXES OF SELENIUM AND TELLURIUM WITH SULFUR-AND SELENIUM CONTAINING LIGANDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 38: 3, 271 — 280

To link to this Article: DOI: 10.1080/03086648808079722

URL: http://dx.doi.org/10.1080/03086648808079722

Phosphorus and Sulfur, 1988, Vol. 38, pp. 271–280
Reprints available directly from the publisher
Photocopying permitted by license only

RECENT DEVELOPMENTS ON THE STRUCTURAL CHEMISTRY OF COMPLEXES OF SELENIUM AND TELLURIUM WITH SULFUR- AND SELENIUM CONTAINING LIGANDS

STEINAR HUSEBYE
Department of Chemistry, University of Bergen,
Bergen, Norway

Abstract The stereochemistry of selenium and tellurium and the role of lone electron pairs will be discussed on the basis of recent X-ray diffraction studies appearing in the literature. Some of the studies represent new types of structures.

INTRODUCTION

The last review on this subject appeared in 1983.[1] Some of the structures presented there and quoted from short communications and unpublished work have now been published in full.[2-7] The title compounds still comprise Se(II), Te(II) and Te(IV) complexes, only. However a regular square planar Se(II) complex has been characterized as have both Te(II) and Te(IV) complexes with two different bidentate ligands bonded to the same central atom. Structures of new complexes of the type $[TeR_2L_2]$, where L is a dithiolate, have been solved.

FOUR-COORDINATE Se(II) COMPLEXES

The structure of $[Se(ptu)_4]Cl_2 \cdot 2HCl$ (ptu = phenylenethiourea) shows for the first time that Se(II) like Te(II) can have a regular centrosymmetric square planar environment.[8] The complex is isomorphous with its Te(II) analog[9] and has an average Se-S bond length of 2.536 Å. This is normal for Se-S in relatively symmetric systems and is 0.33 Å greater than the sum of the respective covalent radii, 2.21 Å. The structure is shown in Fig. 1a. The structure of the sulfur-bridged dimer $[\mathrm{Se_2(ptu)_6}]\mathrm{Br_4} \cdot 10\ \mathrm{H_2O}$,[10] shows that Se(II) is in a distorted, square planar environment, analogous to Te(II) in $[\mathrm{Te_2(etu)_6}]$-$(\mathrm{ClO_4})_4$ (etu=ethylenethiourea).[11] Its structure, shown in Fig. 1b, is also similar to that of $\mathrm{K_2[Se_2(SCN)_6]H_2O}$.[12] The average Se-S bond length is 2.568 Å, a little longer than in the non-bridged complex ion above.

Another type of Se(II) complex is represented by polymeric $[\mathrm{Se}(\bigcirc\mathrm{NCSe_2})\mathrm{I}]_n$.[13] Its structure is similar to that of the tellurium analog, $[\mathrm{Te(EtOCS_2)Br}]_n$,[3] with a distorted square planar, or more correct, a trapezoid planar <u>cis</u>-$\mathrm{SeI_2Se_2}$ coordination sphere, where both halogens are bridging. Average Se-Se and Se-I bond lengths are 2.39 and 3.12 Å, respecctively. They may be compared to the sum of the covalent radii of 2.34 and 2.50 Å. Subtracting the ligand covalent radii from the bond lengths and averaging, gives r_{Se} = 1.51 Å.

The structure of $[\mathrm{Se(Et_2NCS_2)_2}]$ represents a redetermination.[14,15] The average Se-S bond length in this trapezoid planar complex is 2.536 Å, corresponding to r_{Se} = 1.50 Å, close to the value 1.49 Å quoted earlier for such complexes.[1]

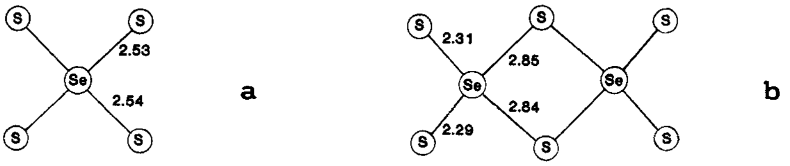

FIGURE 1 The coordination spheres of Se in a, $[\mathrm{Se(ptu)_4}]^{2+}$ and b, $[\mathrm{Se_2(ptu)_6}]^{4+}$

FOUR-COORDINATE Te(II) COMPLEXES

Square-planar complexes with monodentate ligands

These complexes can be subdivided into three groups with coordination spheres A: TeY_4, Y = S or Se, B: TeX_2Y_2 where X is Cl, Br, I and Y = S, C: TeX_3Y, Y = S or Se, X = Cl, Br, I. There are fourteen complexes in group A. Five are of the type $[TeL_4]X_2$ where L represents various thioureas and esu(ethyleneselenourea) and X is Cl^- or ClO_4^-.[9,16-18] Two are of the type trans-$[TeL_2(YCN)_2]$; L = tmtu, Y = S and L = tmsu, Y = Se (tmtu and tmsu = tetramethylthio - and -selenourea).[18] These seven complexes are all centrosymmetric and represent the ++-- isomer which predominate in such complexes.[1,18] A + or - sign indicate that the ligand apart from the S or Se atom lies above or below the coordination plane. There seems to be no steric reasons for this preference. The average Te-S and Te-Se bond lengths are 2.680 and 2.800 Å, corresponding to r_{Te} = 1.64 and 1.63 Å respectively, in excellent agreement with 1.64 Å, the r_{Te} found earlier in similar complexes.[1] This value is 0.27 Å greater than the covalent radius of tellurium and reflects the bond lengthening effect of 3-center 4-electron bonding in such linear Y-Te-Y systems.[1] There are seven complexes of the type cis-$[TeL_2(YCN)_2]$, where L is various thio- and selenoureas and Y = S or Se.[19] In the three isomorphous complexes with L = etu, Y = S; L = esu, Y = S and L = esu, Y = Se, the structure represents the ++++ isomer.

There are seven complexes in group B. Five are monomeric of the type trans-$[TeL_2X_2]$, where L is tmtu or etu and X is Cl, Br and I. The structures of complexes with L = etu and X = Br and I, are redeterminations.[18,20,21] Two polymeric complexes, $\{[Te_2(etu)_4Br_3]_3[TeBr_6]Br\}_n$ and $\{[Te(trtu)_2Br]_2[TeBr_6]\}_n$, where trtu = trimethylenethiourea, have repeating units cis-$[Te(trtu)_2Br_2]$.[22] One of the bromines in the unit is bridging in the first, both are bridging in the second complex. As a result of the bridging and of the trans influence,[1] the TeS_2Br_2 coordination sphere is considerably distorted from square planar geometry. In the trans complexes above, both Te-S and Te-X bonds have average lengths corresponding to r_{Te} = 1.64 Å. In the polymeric cis complexes, the average Te-S bond length is ca. 0.20 Å shorter than in the trans complexes due to trans influence.[1]

Group C consists of six isomorphous dimeric complexes of the type $[TeL_2X_4]$ where L = tmtu or tmsu and X = Cl, Br, I (Fig. 2a).[23] The complexes are centrosymmetric with asymmetric bridges. Two of the structures are redeterminations (Ref. 1. p. 321 and 330).

Trapezoid planar complexes with bidentate ligands

Since the last review, seven $[TeL_2]$ complexes where L is a bidentate ligand, have been structurally characterized.[24-30] L_2 represents $(EtOCS_2^-)_2$, $(i\text{-}prOCS_2^-)_2$, $[(HOCH_2CH_2)_2NCS_2^-]_2$, $(mnt^{2-})_2$, $(Et_2NCS_2^-)(EtOCS_2^-)$, and $(Me_2NCS_2^-)(pap^-)$, where mnt^{2-} = maleonitriledithiolate and pap^- = 2-phenylazophenyl-C,N′. For the first time, such complexes have been prepared with two different bidentate ligands in the same complex.[26,29] The structure of one of these, $[Te(Et_2NCS_2)(EtOCS_2)]$, is shown in Fig. 2b.[26] It illustrates the typical class I trapezoid planar coordination found in complexes with bidentate ligands which are good donors of electrons.[1] An interesting feature of this complex is that the average Te-S bond length for the diethyldithiocarbamate ligand is 0.08 Å shorter than that for the ethylxanthate ligand. Small differences are also found between Te(II) dithiocarbamates and xanthates in this class and indicate that dithiocarbamates are better ligands than xanthates in such complexes.[1,31] However, the average r_{Te} for the above complexes (except $[Te(Et_2NCS_2)(pap)]$[29]) is still close to 1.64 Å. For the first time, the structure of a $[TeL_2]$ complex, where L is a dithiolene, has been solved.[30] In $(Ph_4As)_2[Te(mnt)_2]$, a class I trapezoid planar structure, as shown in Fig. 2c, is found. The average Te-S bond length is 2.76 Å, 0.08 Å longer than the average usually found in such complexes. This is significant and is probably due to the electron withdrawing power of the CN groups which reduces the electron donor capacity of the ligand. The complex [Te{(HOCH$_2$CH$_2$)$_2$NCS$_2$}$_2$] forms an interesting addition compound with [Te{(HOCH$_2$CH$_2$)$_2$NCS$_2$}SCN].[27] There is a weak Te-Te bond of 3.221(3) Å (Sum cov. radii = 2.74 Å), completing the trapezoid planar four-coordination in the latter (Fig. 2d).

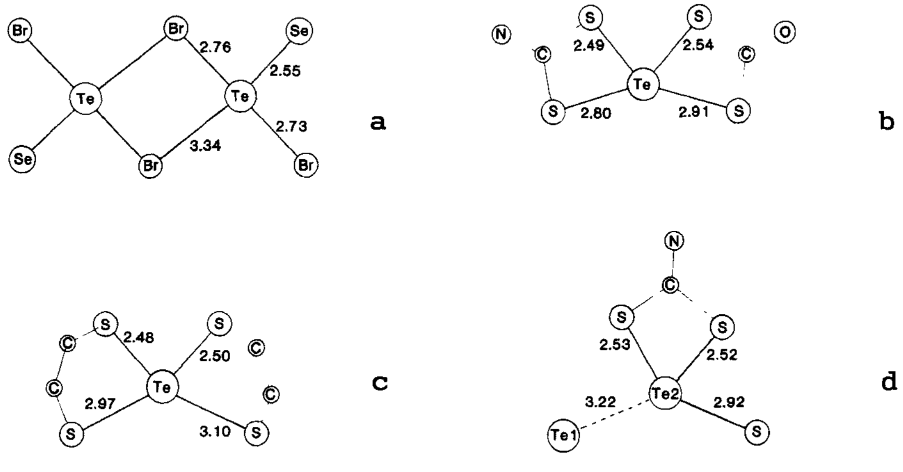

FIGURE 2 The coordination spheres of Te in a, [Te$_2$(tmsu)$_2$Br$_4$] (Triclinic); b, [Te(Et$_2$NCS$_2$)(EtOCS$_2$)]; c, [Te(mnt)$_2$]$^{2-}$; and d, [Te{(HOCH$_2$CH$_2$)$_2$NCS$_2$}(SCN)].

FIVE-COORDINATE, PLANAR Te(II) COMPLEXES

There is only one new complex in this group, [(EtOCS$_2$)$_2$-Te-N⟨O⟩-⟨O⟩N-Te(EtOCS$_2$)$_2$].[32] It may be viewed as two [Te(EtOCS$_2$)$_2$] trapezoid planar complexes weakly linked by the 4,4′-bipyridyl ligand. Appreciable dissociation probably takes place in solution.[22] Bonds and angles are similar to those found in [Te(EtOCS$_2$)$_2$],[24,33] the average Te-S bond length is normal at 2.685 Å. The Te-N bond length at 2.892(8) Å is ca. halfway between the sum of the covalent and van der Waals radii of Te and N. In the only other five-coordinate planar complex, Et$_4$N-[Te(EtOCS$_2$)$_3$], the fifth Te-S bond to a monodentate EtOCS$_2^-$ ligand is the strongest of the five Te-S bonds.[4]

FIVE-COORDINATE Te(IV) COMPLEXES

The complex $[TeBr_2(\underline{p}\text{-}MeOC_6H_4)\{(MeO)_2PS_2\}]$ has a distorted square pyramidal configuration with the *p*-anisyl group apical.[35] A weak intermolecular Te···Br contact approaches the 6th position in an octahedral structure; the lone pair of electrons,(LP), is probably stereochemically active and located near this position.

SIX-COORDINATE Te(IV) COMPLEXES

There are two somewhat similar complexes in this category. $[Te(MeOCS_2)_2(Me)_2]$ and $[Te(Et_2NCS_2)_2(I)(Me)]$ which both have distorted pentagonal pyramidal structures (Fig. 3a).[36,37] The LP is stereochemically active and makes the complexes Ψ-pentagonal bipyramidal.

Another type of structure is found in the six complexes $[Te(Ph)_2\{(MeO)_2PS_2\}_2]$,[35] and $[Te(Ph)_2\{(EtO)_2PS_2\}_2]$, $[Te(Ph)_2(Et_2NCS_2)_2]$, $[Te(C_8H_8)(Et_2NCS_2)_2]$, $[Te(C_8H_8)(I)(Et_2NCS_2)]$, $[Te\{OTe(C_8H_8)((EtO)_2PS_2)\}_6]$.[37] In these complexes, the central Te(IV) atom is bonded to six other atoms and the arrangement may be described as very distorted octahedral (Fig. 3b). However, the LP is probably stereochemically active in all six and the best description is probably in terms of pseudo seven-coordination, where these complexes adopt a Ψ - 1:2:2:2 structure.[37] This structure ideally has $\underline{C}2$ symmetry and represents a considerable distortion from pentagonal bipyramidal symmetry.[38,39]

SEVEN-COORDINATE Te(IV) COMPLEXES

There are two complexes with inert LPs, $[Te\{(HOCH_2CH_2)_2NCS_2\}_3X]$, where X = Cl^- and SCN^-.[40,41] They have the normal small S-S "bite" distorted pentagonal bipyramidal configuration with X axial.[1] The complex $[Te\{(HOCH_2CH_2)_2NCS_2\}_2I_2]$ also has a pentagonal bipyramidal structure.[42] Here the two iodines are axial. The equatorial Te-I bond is weak and intermolecular with a bond length of 3.427(2) Å (The sums of the covalent and van der Waals radii are 2.70 and 4.04 Å, respectively). The neighbour equatorial Te-S bonds are significantly longer than the other Te-S bonds and the structure may alternatively be described as Ψ-pentagonal bipyramidal with the LP active[42] and located near the equatorial Te-I contact. The coordination spheres in the three complexes $[Te(C_8H_8)(EtOCS_2)_2]$, $[Te(C_8H_8)\{(EtO)_2PS_2\}_2]$, and $[Te(Ph)(Et_2NCS_2)_2\{(EtO)_2PS_2\}]$, are similar,[37] and also similar to that of $[Te(Ph)(Et_2NCS_2)_3]$.[43] These structures may at a first glimpse be described as distorted pentagonal bipyramidal with the main distortion caused by a weak, skewed Te-S interaction which is intermolecular for the first two complexes and intramolecular in the two others. The structure of the mixed dithiolate complex is shown in Fig. 3c. In this description the trans influence of an aryl (or alkyl) group causes some distortion and the role of the LP is unclear.[43] An alternative description of these complexes as distorted dodecahedral with an active LP seems plausible.[37]

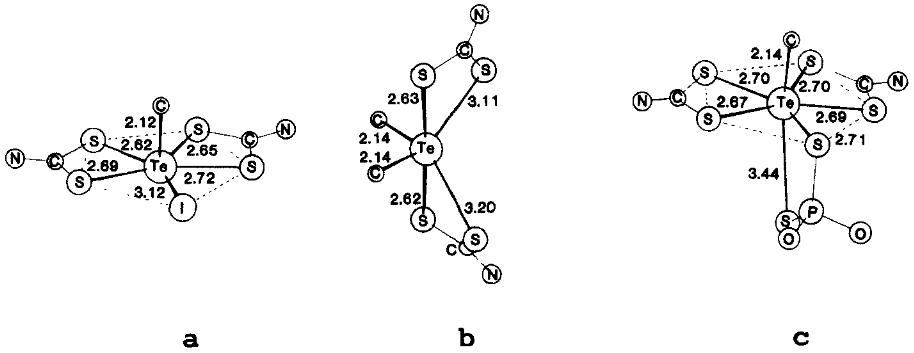

FIGURE 3 The coordination spheres of Te in a, $[Te(Et_2NCS_2)_2(I)(Me)]$; b, $[Te(Ph)_2(Et_2NCS_2)_2]$; and c, $[Te(Ph)(Et_2NCS_2)_2\{(EtO)_2PS_2\}]$.

EIGHT-COORDINATE Te(VI) COMPLEXES

The only structure solved in this category is that of $[Te\{(HOCH_2CH_2)_2NCS_2\}_4]$.[44] It has the normal dodecahedral structure with an inert LP.[1]

CONCLUDING REMARKS

The two LPs are stereochemically active in Se(II) and Te(II) complexes, being located above and beneath the coordination plane. In Te(IV) complexes the LP is always stereochemically active for coordination numbers less than six. For numbers six and seven it is sometimes active and sometimes inert and for coordination number eight it is always inert.[1] However, inert lone pairs in the VSEPR sense probably are antibonding.[1,45] Extensive solution NMR studies indicate that Te(IV) complexes with sulfur containing ligands often retain their structures in solution.[37] They further indicate that such complexes are labile with respect to ligand exchange. It also appears that bidentate, dithiolate ligands may be ranked as nucleophiles in the order $R_2NCS_2^- > EtOCS_2 > [(EtO)_2PS_2^-]$ based on bond lengths found in Se and Te complexes. This is supported by other work.[46,47]

Bonding in Se and Te complexes have been discussed in a recent review.[1] The present work support the idea of covalent radii for the divalent elements participating in 3-center 4-electron systems being close to 1.50 and 1.64 Å, respectively. Bonding and structure in tellurium complexes are also discussed by Burdett.[48]

In the present work, weak secondary bonds have in most cases been taken into consideration in the description of the structures; covalent and van der Waals radii are taken from Pauling and Bondi, respectively (Ref. 1, Table 1).

REFERENCES

1. S. Husebye, in Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium, edited by F. J. Berry and W. R. McWhinnie (The University of Aston, Birmingham, England, 1983) pp. 298-378.
2. S. Hauge and O. Vikane, Acta Chem. Scand., Ser. A39, 553 (1985).
3. R. W. Gable, B. F. Hoskins, R. J. Steen, and G. Winter, Inorg. Chim. Acta, 72, 173 (1983).
4. S. V. Bjørnevåg and S. Hauge, Acta Chem. Scand., Ser. A37, 235 (1983).
5. S. Husebye and K. Maartmann-Moe, Acta Chem. Scand., Ser. A37, 219 (1983).
6. L. Refaat, K. Maartmann-Moe and S. Husebye, Acta Chem. Scand., Ser. A38, 147 (1984)
7. L. Refaat, K. Maartmann-Moe and S. Husebye, Acta Chem. Scand., Ser. A38, 303 (1984).
8. S. Sowrirajan, G. Aravamudan, M. Seshasayee, and G. C. Rout, Acta Crystallogr., Sect. C41, 576 (1985).
9. G. C. Rout, M. Seshasayee, G. Aravamudan, and S. Sowrirajan, Polyhedron, 3, 921 (1984).
10. Sp. Chidambaram, G. Aravamudan, G. C. Rout, and M. Seshasayee, Can. J. Chem., 64, 477 (1986).
11. A. Foust, Inorg. Chem., 19, 1050 (1980).
12. S. Hauge and P. A. Henriksen, Acta Chem. Scand., Ser. A29, 778 (1975).
13. F. Bigoli, E. Leporati, M. A. Pellinghelli, G. Crisponi, P. Deplano, and E. Trogu, J. Chem. Soc., Dalton Trans., 1763 (1983).
14. A. Sugihara, Kagaku to Kogyo, 59, 319 (1985).
15. S. Husebye and G. Helland-Madsen, Acta. Chem. Scand., 24, 2273 (1970).
16. G. C. Rout, M. Seshasayee, G. Aravamudan, and S. Sowrirajan, Acta Crystallogr., Sect. C40, 963 (1984).
17. G. C. Rout, M. Seshasayee, G. Aravamudan, and S. Sowrirajan, J. Cryst. Spectrosc. Res., 15, 377 (1985).
18. O. Foss, K. Maartmann-Moe, and K. Marøy, Acta. Chem. Scand., Ser. A40, 685 (1986).
19. O. Foss, J. Henjum, K. Maartmann-Moe, and K. Marøy, Acta. Chem. Scand., Ser. A41, 77 (1987).
20. O. Foss, H. M. Kjøge, and K. Marøy, Acta. Chem. Scand., 19, 2349 (1965).
21. O. Foss and K. Maartmann-Moe, Acta. Chem. Scand., Ser. A40, 675 (1986).
22. O. Foss, K. Maartmann-Moe, and K. Marøy, Acta. Chem. Scand., Ser. A40, 669 (1986).
23. J. Eide, O. Foss, K. Maartmann-Moe, O. Maberg, and A. Scheie, Acta. Chem. Scand., Ser. A41, 67 (1987).

24. E. R. T. Tiekink, Acta Crystallogr., Sect. C42, 633 (1986).
25. B. F. Hoskins, E. R. T. Tiekink, and G. Winter, Inorg. Chim. Acta, 96, L79 (1985).
26. B. F. Hoskins, E. R. T. Tiekink, and G. Winter, Inorg. Chim. Acta, 105, 171 (1985).
27. K. Radha, G. Aravamudan, A. Rajalakshmi, G. C. Rout, and M. Seshasayee, Aust. J. Chem., 39, 847 (1986)
28. G. C. Rout, M. Seshasayee, K. Radha, and G. Aravamudan, Acta Crystallogr., Sect. C39, 1021 (1983).
29. M. A. K. Ahmed, A. E. McCarthy, W. R. McWhinnie, and F. J. Berry, J. Chem. Soc. Dalton Trans., 771 (1986).
30. W. Dietsch, (Sektion Chemie, Karl-Marx-Universität, Leipzig, D. D. R.). Private communication.
31. O. Foss, Acta Chem. Scand., 3, 1385 (1949).
32. B. F. Hoskins, P. Oliver, and G. Winter, Inorg. Chim. Acta, 86, L21 (1984).
33. S. Husebye, Acta Chem. Scand., 21, 42 (1967).
34. B. F. Hoskins, C. D. Pannan, Aust. J. Chem., 29, 2337 (1967).
35. R. K. Chadha, J. E. Drake, N. T. McManus, B. A. Quinlan, and A. B. Sarkar, Organometallics, 6, 813 (1987).
36. M. Wieber, E. Schmidt, and Ch. Burschka, Z. anorg. allg. Chem., 525, 127 (1985).
37. D. Dakternieks, (Chemical & Physical Sciences, Deakin University, Victoria 3217, Australia). Private communication. Di Giacomo, R., Ph. D. Thesis, (University of Melbourne, Victoria 3052, Australia, 1987).
38. T. A. Claxton and G. C. Benson, Can. J. Chem., 44, 157 (1966).
39. H. B. Thompson and L. S. Bartell, Inorg. Chem., 7, 488 (1968).
40. G. V. N. Appa Rao, M. Seshasayee, G. Aravamudan, and K. Radha, Inorg. Chem., 22, 2590 (1983).
41. G. C. Rout, M. Seshasayee, G. Aravamudan, and K. Radha, J. Cryst. Spectrosc. Res., 14, 193 (1984).
42. G. V. N. Appa Rao, M. Seshasayee, G. Aravamudan, and K. Radha, Acta Crystallogr., Sect. C39, 1018 (1983).
43. E. Esperås and S. Husebye, Acta Chem. Scand., 26, 3293 (1972).
44. G. C. Rout, M. Seshasayee, G. Aravamudan, and K. Radha, Acta Crystallogr., Sect. C40, 1142 (1984).
45. M. G. B. Drew and D. G. Nicholson, J. Chem. Soc. Dalton Trans, 1543 (1986).
46. J. Willemse, J. A. Cras, J. J. Steggerda, and C. P. Keijzers, Struct. and Bonding (Berlin), 28, 83 (1976).
47. S. V. Larionov, A. A. Voityuk, N. Mazalov, A. I. Shpon'ko, V. D. Yumatov, and S. B. Erenburg, Izvest. Akad. Nauk SSSR, Ser. Khim. 998 (1981).
48. J. K. Burdett, Molecular Shapes, (J. Wiley & Sons, New York, 1980), p. 64.