Investigation into Aroylhydrazones as Chelating Agents. Synthesis and Structural Characterization of a Tin(IV) Complex with 2,6-Diacetylpyridine Bis(salicyloylhydrazone)

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2,6-Diacetylpyridine bis(salicyloylhydrazone) (H_2daps) has been synthesized and its co-ordinating properties have been investigated in the complex [SnPr$^n_2$(daps)] by means of spectroscopic (i.r. and u.v.) and *X*-ray diffractometric techniques. Crystals of the compound are orthorhombic, with $a = 18.332(10)$, $b = 17.187(11)$, $c = 9.161(5)$ Å; $Z = 4$, space group $P2_12_12_1$. A total of 1 936 observed reflections have been measured by single-crystal diffractometry and refined by full-matrix least squares to R 0.0402. The quinquedentate behaviour and the near planarity of the organic ligand favours a pentagonal-bipyramidal arrangement around tin with the two propyl groups occupying the axial sites.

THE condensation products of 2,6-diacetylpyridine with organic molecules such as diamines or hydrazides have been found to adopt a pentagonal-bipyramidal stereochemistry in various metal complexes, where they may take part in the neutral and/or dianionic form.[1-7]

We have previously examined the chelating behaviour of aroylhydrazones of some aromatic aldehydes towards metal ions with the aim of investigating the influence co-ordination exerts on the conformation and the geometry of the organic molecule in relation to the nature of the metal and of the inorganic anion.[8-12] Among these ligands, the behaviour of 2,6-diacetylpyridine bis(picolinoylhydrazone) (H_2dappc) is noteworthy for its remarkable versatility as a chelating agent and for its tendency to produce stereochemistries with high co-ordination numbers.[11,12] Moreover, it can undergo cyclization by reaction with diamines to form quinquedentate *NNNNN* macrocycles, reactions of this type being in progress in our laboratory with di- and tri-valent transition-metal ions. For this reason it seemed interesting to investigate 2,6-diacetylpyridine aroylhydrazones, varying the geometry, the flexibility, and the nature of the donor atoms. Thus, 2,6-diacetylpyridine bis(salicyloylhydrazone) (H_2daps) has been synthesized and its co-ordinating properties investigated in an organotin(IV) complex of formula [SnPr$^n_2$(daps)].

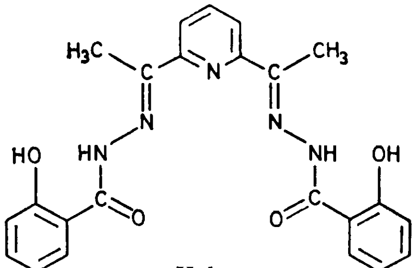
This paper deals with the synthesis, the vibrational and electronic spectra of both H_2daps and [SnPr$^n_2$(daps)], and the *X*-ray crystal structure of the tin complex.

EXPERIMENTAL

Preparation of H_2daps.—Salicylhydrazide and 2,6-diacetylpyridine (2 : 1 mole ratio) in a 1 : 1 ethanol–benzene mixture were heated under reflux for 1 h. During this time, an almost insoluble cream product is formed slowly. After cooling, partial evaporation of the solvent was effected and the crude product filtered off. The compound is sparingly soluble in acetone, from which recrystallization yields a microcrystalline compound with melting point 234 °C (Found: C, 63.7; H, 4.9; N, 15.8. $C_{23}H_{21}N_5O_4$ requires C, 64.0; H, 4.9; N, 16.2%).

Preparation of [SnPr$^n_2$(daps)].—Di-n-propyltin dichloride in anhydrous acetone was added, under a nitrogen atmosphere, to a boiling suspension of H_2daps in dry methanol and allowed to reflux for several minutes. After some days, by slow evaporation of the solvent, gold-yellow prisms separated out. Experimental chemical analyses are in agreement with the formula $Sn(C_3H_7)_2(C_{23}H_{19}N_5O_4)$, where both chlorine atoms are substituted by the organic ligand in its deprotonated form. The same compound was also obtained from the reaction of tri-n-propyltin chloride with H_2daps under similar reaction conditions (Found: C, 55.1; H, 5.4; N, 10.8. $C_{29}H_{33}N_5O_4Sn$ requires C, 54.9; H, 5.2; N, 11.0%).

Crystal and Molecular Structure Determination of [SnPr$^n_2$(daps)].—Weissenberg photographs taken with Cu-K_α radiation showed the space group to be $P2_12_12_1$. A small crystal, whose shape was that of an elongated prism, was chosen for diffraction work and centred on an on-line Siemens AED diffractometer. The unit-cell parameters were obtained by a least-squares fit to the carefully measured values of 15 strong reflections. Crystal data are as follows: $C_{29}H_{33}N_5O_4Sn$, Orthorhombic, $M = 634.30$, $a = 18.332(10)$, $b = 17.187(11)$, $c = 9.161(5)$ Å, $U = 2\,886(3)$ Å^3, $D_m = 1.480$ g cm^{-3}, $Z = 4$, $D_c = 1.460$, $F(000) = 1\,296$, μ(Mo-K_α) = 9.27 cm^{-1}.



H_2daps

Intensity data were collected up to $2\theta = 50.0°$ by use of niobium-filtered Mo-K_α radiation ($\lambda = 0.710\,69$ Å) in the ω—2θ scan mode with the take-off angle set to 4°. Equivalent reflections were averaged and those systematically absent were removed to give 2 890 independent reflections, of which 1 936 had $I \geqslant 2\sigma(I)$ and were used in crystal analysis. Reflections with counting rates greater than 9 000 counts s^{-1} were automatically attenuated by insertion of metal foils into a path of the diffracted beam until the intensity was reduced to less than that value. Crystal and instrument stability were monitored throughout by remeasuring the intensity of a standard reflection (462) after every 20 measurements. The intensity of the check reflection remained constant to within ±2% during data collection. Intensities were converted to unscaled F_o values after correction for Lorentz and polarization effects. No absorption correction was made because the crystal had a relatively low absorption coefficient and was small and of approximately isotropic shape.

Table 1

Fractional atomic co-ordinates ($\times 10^4$) for [SnPr$^n_2$(daps)] with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Sn(1)	615(1)	2 762(1)	1 062(1)
O(1)	1 097(5)	−384(5)	2 550(11)
O(2)	1 407(4)	2 011(4)	2 350(9)
O(3)	1 428(4)	3 757(4)	1 159(10)
O(4)	1 044(8)	5 817(6)	−1 161(15)
N(1)	619(5)	974(5)	2 074(9)
N(2)	176(4)	1 505(5)	1 401(9)
N(3)	−549(5)	2 596(5)	68(10)
N(4)	184(5)	3 859(5)	−125(10)
N(5)	634(6)	4 496(5)	−201(11)
C(1)	1 745(6)	768(6)	3 233(12)
C(2)	1 679(6)	−37(7)	3 152(14)
C(3)	2 212(8)	−514(7)	3 736(15)
C(4)	2 787(8)	−174(11)	4 493(17)
C(5)	2 856(7)	615(10)	4 606(16)
C(6)	2 352(6)	1 071(7)	3 985(15)
C(7)	1 227(6)	1 294(6)	2 496(12)
C(8)	−467(6)	1 280(6)	939(14)
C(9)	−726(7)	458(8)	1 082(21)
C(10)	−891(6)	1 907(8)	197(13)
C(11)	−1 593(6)	1 792(10)	−316(15)
C(12)	−1 931(7)	2 408(10)	−1 002(19)
C(13)	−1 573(6)	3 092(9)	−1 171(15)
C(14)	−879(6)	3 184(8)	−625(12)
C(15)	−442(6)	3 885(7)	−767(13)
C(16)	−757(13)	4 571(13)	−1 475(25)
C(17)	1 247(7)	4 395(6)	530(13)
C(18)	1 759(7)	5 056(7)	557(14)
C(19)	1 643(11)	5 717(9)	−272(21)
C(20)	2 129(15)	6 343(11)	−157(26)
C(21)	2 734(13)	6 223(11)	716(26)
C(22)	2 868(9)	5 607(9)	1 528(21)
C(23)	2 372(8)	4 983(8)	1 415(17)
C(24)	1 174(8)	2 423(8)	−894(17)
C(25)	811(9)	1 867(10)	−1 904(21)
C(26)	1 242(10)	1 704(11)	−3 271(22)
C(27)	231(9)	3 188(10)	3 084(19)
C(28)	−235(12)	2 692(14)	4 001(28)
C(29)	−441(14)	3 072(15)	5 455(32)
H(1)	724(72)	−48(69)	3 164(136)
H(2)	2 157(65)	−1 138(72)	3 663(141)
H(3)	3 183(73)	−596(80)	4 780(151)
H(4)	3 339(72)	864(73)	4 980(137)
H(5)	2 376(62)	1 595(72)	4 271(160)
H(6)	−731(85)	319(76)	14(159)
H(7)	−1 260(68)	482(68)	1 306(137)
H(8)	−311(66)	30(69)	1 123(160)
H(9)	−1 777(52)	1 238(60)	−389(105)
H(10)	−2 482(57)	2 346(63)	−1 405(129)
H(11)	−1 862(53)	3 585(58)	−1 549(109)
H(12)	−498(66)	4 750(73)	−2 121(153)
H(13)	−563(67)	5 008(72)	−885(143)
H(14)	−1 260(79)	4 453(85)	−1 814(177)
H(16)	2 037(61)	6 887(73)	−717(137)
H(17)	3 010(64)	6 716(73)	944(146)
H(18)	3 265(71)	5 352(83)	1 794(161)
H(19)	2 473(67)	4 448(69)	2 001(135)

The structure was solved by the heavy-atom technique; the position of the tin atom was obtained from a Patterson map. An electron-density map phased on the refined tin co-ordinates yielded 15 out of the 38 non-hydrogen atoms. Further isotropic refinement with all these atoms followed by another ΔF map resulted in the location of the remaining non-hydrogen atoms. Full-matrix least-squares refinement, in which $\Sigma w(F_o - F_c)^2$ was minimized, led to R 0.067 1, which dropped to 0.051 5 when anisotropic thermal parameters were introduced. Whilst most hydrogen-atom positions could be determined from a difference map, any attempt to locate the hydrogen atom on O(4) or those belonging to the propyl groups was unsuccessful. One more cycle of refinement including hydrogen atoms with isotropic thermal parameters reduced R to 0.040 2.

Considering the satisfactory adjustment between F_o and F_c at low diffraction angles it was not found necessary to apply a secondary extinction parameter. The function minimized was $\Sigma w|\Delta F^2|$; unit weights were used at first, and in the last cycles of refinement the weighting scheme $w = [\sigma^2(F_o) + 0.005|F_o|^2]^{-1}$ was employed and found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $(\sin\theta)/\lambda$ and with increasing fractions of F_o. A final difference synthesis showed no peak higher than 0.26 e Å^{-3}.

Final atomic co-ordinates are given in Table 1. Lists of thermal parameters and structure factors are given in Supplementary Publication No. SUP 22793 (14 pp.).* Calculations were performed using programs of the SHELX 76 System.[13] Complex neutral-atom scattering factors and anomalous-dispersion corrections were taken from ref. 14.

All calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, with financial support of the University of Parma.

RESULTS AND DISCUSSION

Electronic Spectra.—Electronic spectra of ethanol solutions of H$_2$daps and of [SnPr$^n_2$(daps)] were recorded in the 20×10^3—50×10^3 cm^{-1} range. Both the compounds show a quite similar pattern in that there are two main absorption maxima. The low-energy bands show lower molar absorption coefficients {41.3×10^3—43.1×10^3 cm^{-1}, $\varepsilon = 9\,200$ dm^3 mol^{-1} cm^{-1} for H$_2$daps; 40×10^3 cm^{-1}, $\varepsilon = 6\,400$ dm^3 mol^{-1} cm^{-1} for [SnPr$^n_2$-

Table 2

Selected vibrational bands (cm^{-1}) of H$_2$daps and [SnPr$^n_2$(daps)]

H$_2$daps	[SnPr$^n_2$(daps)]	Assignment
3 300 (sh)		ν(NH)
3 200br, m		ν(NH)
3 080 (sh)	3 080mw	ν(CH)
	3 050mw	ν(CH)
2 920m	2 960ms	ν(CH)
2 850m	2 860m	ν(CH)
2 700br, m	2 100—2 300br, m	ν(OH)
2 560br		ν(OH)
1 695 (sh)		
1 650vs	1 640m	ν(CO)
1 610s	1 595s	Ring
	1 580 (sh)	
1 500vs	1 550vs	ν(CN) + Ring
	1 520s	Ring
1 495m	1 488s	Ring
1 455s	1 450s	Ring
	550mw	ν(SnC)
	535m	
	405ms	ν(SnO)

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 3
Selected bond distances (Å) and angles (°) for [SnPr$^n_2$(daps)]

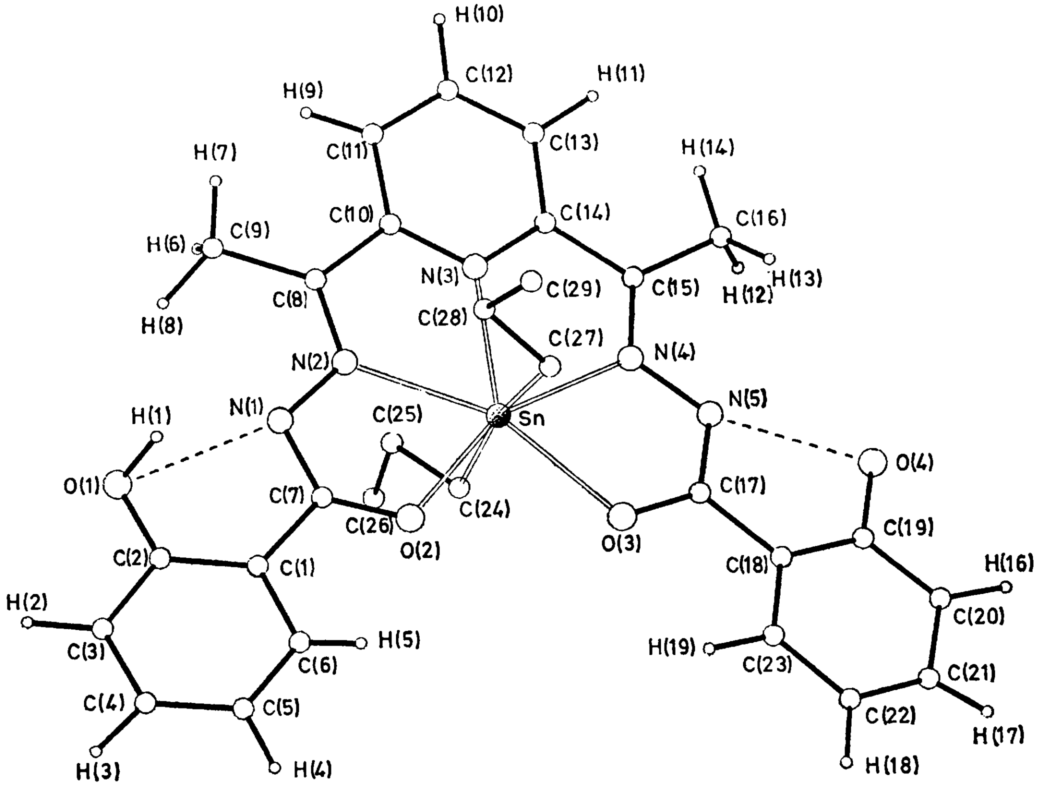
Sn–O(2)	2.273(6)	N(3)–C(14)	1.34(1)
Sn–O(3)	2.270(7)	N(4)–N(5)	1.37(1)
Sn–N(2)	2.326(8)	N(4)–C(15)	1.29(2)
Sn–N(3)	2.337(8)	N(5)–C(17)	1.32(2)
Sn–N(4)	2.315(9)	C(1)–C(7)	1.47(2)
Sn–C(24)	2.14(1)	C(8)–C(9)	1.50(2)
Sn–C(27)	2.11(1)	C(8)–C(10)	1.49(2)
O(1)–C(2)	1.34(2)	C(14)–C(15)	1.45(2)
O(2)–C(7)	1.28(1)	C(15)–C(16)	1.46(3)
O(3)–C(17)	1.28(1)	C(17)–C(18)	1.47(2)
O(4)–C(19)	1.38(3)	C(24)–C(25)	1.49(2)
N(1)–N(2)	1.37(1)	C(25)–C(26)	1.51(3)
N(1)–C(7)	1.30(1)	C(27)–C(28)	1.47(3)
N(2)–C(8)	1.31(2)	C(28)–C(29)	1.53(4)
N(3)–C(10)	1.34(2)		
O(2)–Sn–O(3)	89.3(2)	Sn–O(3)–C(17)	117.2(7)
O(2)–Sn–N(2)	67.9(3)	N(2)–N(1)–C(7)	111.1(8)
O(2)–Sn–N(3)	135.7(3)	Sn–N(2)–N(1)	118.3(6)
O(2)–Sn–N(4)	157.5(3)	Sn–N(2)–C(8)	122.8(8)
O(2)–Sn–C(24)	88.5(4)	N(1)–N(2)–C(8)	118.8(9)
O(2)–Sn–C(27)	87.4(5)	Sn–N(3)–C(10)	119.9(7)
O(3)–Sn–N(2)	157.1(3)	Sn–N(3)–C(14)	120.3(7)
O(3)–Sn–N(3)	134.9(3)	Sn–N(4)–C(15)	123.1(8)
O(3)–Sn–N(4)	68.2(3)	Sn–N(4)–N(5)	117.9(7)
O(3)–Sn–C(24)	85.6(4)	N(5)–N(4)–C(15)	118.9(10)
O(3)–Sn–C(27)	85.6(5)	N(4)–N(5)–C(17)	112.4(9)
N(2)–Sn–N(3)	67.8(3)	N(1)–C(7)–O(2)	126.5(9)
N(2)–Sn–N(4)	134.5(3)	C(9)–C(8)–C(10)	123.8(13)
N(2)–Sn–C(24)	91.4(4)	N(2)–C(8)–C(10)	113.7(11)
N(2)–Sn–C(27)	95.1(5)	N(2)–C(8)–C(9)	122.4(13)
N(3)–Sn–N(4)	66.7(3)	N(4)–C(15)–C(14)	114.9(11)
N(3)–Sn–C(24)	94.4(5)	C(14)–C(15)–C(16)	119.4(14)
N(3)–Sn–C(27)	94.6(5)	N(4)–C(15)–C(16)	125.3(14)
N(4)–Sn–C(24)	89.5(5)	O(3)–C(17)–N(5)	124.1(10)
N(4)–Sn–C(27)	90.9(5)	Sn–C(24)–C(25)	118.7(11)
C(24)–Sn–C(27)	170.4(6)	Sn–C(27)–C(28)	119.6(14)
Sn–O(2)–C(7)	115.8(6)		

(daps)]}. The high-energy bands {31.5×10^3—32.9×10^3 cm^{-1}, ε = 12 000 dm^3 mol^{-1} cm^{-1} for H$_2$daps; 28.3×10^3—29.5×10^3 cm^{-1}, ε = 13 000 dm^3 mol^{-1} cm^{-1} for [SnPr$^n_2$(daps)]} can be attributed to the wide chromophore system, which increases its delocalisation upon co-ordination. A shoulder at *ca.* 24.4×10^3 cm^{-1} is probably due to a charge-transfer metal–ligand transition.

Infrared Spectra.—The most significant differences which emerge from a comparison of the vibrational absorptions of the free organic ligand with those of the complex (Table 2) can be summarised as follows: (i) disappearance of the ν(NH) band as a consequence of the dianionic nature which H$_2$daps assumes upon co-ordination; (ii) lowering of the frequency and absorption intensity for the carbonyl stretching band, which is influenced by the co-ordination through the oxygen atom and by the deprotonation of the two C(O)NH groups [the ν(CN) value seems to be unchanged at 1 550 cm^{-1} upon co-ordination]; and (iii) shift of the broad ν(OH) band towards lower frequency in accord with the presence of OH · · · N hydrogen bonds, as found by *X*-ray analysis.

The vibrational bands involving the tin atom mainly refer to Sn–O [15] and Sn–C [16] bonds, while for the ν(Sn–N) band assignment is rather difficult. The multiple character of the ν(Sn–C) absorption is justified by the presence in the complex of two propyl groups σ-bonded to tin.

X-*Ray Structure of* [SnPr$^n_2$(daps)].—A perspective view of the molecular structure, which includes the



Projection of the structure of [SnPr$^n_2$(daps)] numbering scheme used in the Tables and in the following discussion, is depicted in the Figure. The tin atom is seven-co-ordinate, being bonded to three nitrogen atoms and two oxygen atoms of the organic ligand and to a carbon atom in each of the two n-propyl groups in a pentagonal-bipyramidal arrangement. This structure is a further example of the preference shown by the seven-co-ordinate tin for the pentagonal-bipyramidal geometry,[17] which in our compound is a direct result of the tendency of the organic molecule to function as planar quinquedentate ligand. The complex is, to our knowledge, the first example of a seven-co-ordinate tin complex having in the pentagonal girdle atoms of different types (*i.e.* nitrogens and oxygens).

Selected interatomic distances and angles are given in Table 3. Individual values within the aromatic rings have not been listed as they are of no consequence and are not used in the subsequent discussion [the C–C distances range from 1.32 to 1.41 Å, mean 1.38(2) Å]. This is the first structural study of a metal complex of H_2daps, so no direct comparison of the bond distances at tin, which however appear to be unremarkable, and of ligand geometry can be made. With regard to this last aspect, the similarity between H_2daps and H_2dappc should be noted; they are both characterized by the presence of two $C(O)N^1N^2CCN^3$ chelating systems having the N^3 pyridinic nitrogen in common. Moreover, if we restrict the comparison to [SnPr$^n_2$(daps)] and [Mn(H_2dappc)Cl_2]·$5H_2O$ [12] the similarity between the two ligands goes further and involves the quinquedentate behaviour, the nature of the donor atoms, the chelation rings, and the overall geometry of the complex. The sole difference concerns the deprotonation of the ligand which only occurs in the tin compound.

The group of five equatorial atoms deviates slightly, but significantly, from planarity, the maximum deviation from the best least-squares plane being 0.04 Å. The tin atom lies in this plane and is 0.18 Å off the straight line running through the apical carbon atoms [C–Sn–C 170.4(6)°]. This line is nearly perpendicular to the equatorial plane, the angle it makes with the plane being 89.4°.

Least-squares planes drawn through the individual chelation rings show maximum deviations from planarity of 0.040 Å for N, 0.033 Å for O, 0.037 Å for C, and 0.001 Å for Sn.

Comparison of bond lengths in the C(O)NNCCN chelating system found in the present compound and in the H_2dappc derivatives (Table 4) shows that they are scarcely influenced by the nature of the ligand and by its co-ordinating behaviour. The only significant differences concern the C(O)N group which shows higher π delocalization in [SnPr$^n_2$(daps)], in which the system is deprotonated and the oxygen atom is involved in the co-ordination to metal.

The two phenolic oxygen atoms are hydrogen bonded to the two adjacent nitrogen atoms: O(1) · · · N(1) 2.53(1); O(4) · · · N(5) 2.55(2) Å. There are no unacceptably short intermolecular contacts, the shortest being 3.33(2) Å between atom C(5) of one phenyl ring and atom O(1) of a phenolic group on a neighbouring molecule.

TABLE 4

Comparison of bond lengths (Å) in the chelating $C(O)N^1N^2CCN^3$ system

	O–C	C–N^1	N^1–N^2	N^2–C	C–C	C–N^3
H_2dappc [a]	1.221(5) 1.217(4)	1.357(5) 1.359(4)	1.375(4) 1.376(4)	1.288(5) 1.285(4)	1.489(5) 1.486(5)	1.341(5) 1.348(4)
[Cu_2(dappc)Cl_2]·H_2O [b]	1.242(6) 1.254(5)	1.336(6) 1.340(5)	1.399(5) 1.382(5)	1.290(6) 1.296(6)	1.469(6) 1.483(6)	1.343(5) 1.337(5)
[Mn(H_2dappc)Cl_2]·$5H_2O$ [c]	1.236(12) 1.217(11)	1.345(14) 1.374(14)	1.364(12) 1.378(12)	1.299(15) 1.299(15)	1.496(14) 1.505(14)	1.334(13) 1.321(12)
[SnPr$^n_2$(daps)]	1.283(11) 1.282(13)	1.302(13) 1.320(15)	1.368(11) 1.373(13)	1.311(15) 1.290(16)	1.492(19) 1.453(18)	1.345(16) 1.338(14)

[a] Ref. 18. [b] Ref. 11. [c] Ref. 12.

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