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Synthesis and Crystal and Molecular Structure of New (*N*,*N*-Di-*n*-propylthiocarbamato)palladium(II) Compounds

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The reaction of sodium chloropalladate(II) with potassium *N*,*N*-di-*n*-propylthiocarbamate, $K(SCONR_2)$, affords $Pd_2(SCONR_2)_4$ (A) or $NaHPd(SCONR_2)_4$ (D) depending on the metal to ligand ratio. D is converted to *trans*-$Pd(SCONR_2)_2(NHR_2)_2$ (B) in 2-propanol. Reactions of A, B, and D with triphenylphosphine convert these into *trans*-$Pd(SCONR_2)_2(PPh_3)_2$ (C). The structures of B–D have been determined by X-ray diffraction. D ($C_{28}H_{57}N_4NaO_4PdS_4$, monoclinic, $a = 14.953$ (3) Å, $b = 15.244$ (9) Å, $c = 16.968$ (4) Å, $\beta = 98.70$ (2)°, $Z = 4$, $P2_1/n$) is a dimer with Pd in a planar PdS_4 environment. The two sodium atoms are hexacoordinated, and two $NaO_5(Pd)$ polyhedra are joined by two oxygen atoms via an inversion center. The structure of C ($C_{50}H_{58}N_2O_2P_2PdS_2$, monoclinic, $a = 9.847$ (2) Å, $b = 20.454$ (7) Å, $c = 12.215$ (3) Å, $\beta = 101.19$ (2)°, $Z = 2$, $P2_1/n$) contains two sulfur-bound monodentate R_2NCOS ligands in a trans arrangement. Hydrogen bonding between the H atoms of the diisopropylamine ligands on the carbonyl oxygen atoms has been detected in the structure of B ($C_{26}H_{58}N_4O_2PdS_2$, triclinic, $a = 9.196$ (7) Å, $b = 9.982$ (9) Å, $c = 10.682$ (10) Å, $\alpha = 86.79$ (7)°, $\beta = 74.64$ (7)°, $\gamma = 64.80$ (7)°, $Z = 1$, $P\bar{1}$).

Introduction

The coordination chemistry of dithiocarbamate ligands is extensive[1,2] and continues to attract considerable attention. Synthetic and structural studies on monothiocarbamate (mtc) complexes are at a much less advanced stage although many compounds have been prepared and characterized as demonstrated by a recent review.[3] While dithiocarbamates (dtc) usually function as bidentate chelating ligands,[4] there is a wider variety of bonding modes for mtc derivatives. So far, four types of bonding can be distinguished,[3-5] viz. (i) monodentate through the sulfur atom, (ii) bidentate through the sulfur and oxygen atoms, (iii) bidentate, with the sulfur atom bridging neighboring metal ions, and (iv) sulfur-bridging monodentate. The mtc complexes of group VIII metals, especially those of the nickel triad, have been studied more extensively than those of other metals.[3] The structural information available has been derived from infrared and ^{13}C NMR data for Pd and Pt complexes,[3-5] and X-ray structures are available for $Ni(mtc)_2$ (di-*n*-propyl and di-*n*-butyl derivatives, respectively), which have been found to be cyclic hexamers.[3,6,7] Furthermore, four X-ray structures of tin pyrrolidinecarbothioate complexes have been determined recently.[8] Thus, it is difficult to predict the structure of these complexes. Furthermore, we observed that a number of different compounds were obtained in an attempt to prepare $Pd[S(O)CN(C_3H_7)_2]_2$. This prompted a more detailed study, and we report the synthesis and structures of four new palladium(II) complexes with the ligand *N*,*N*-di-*n*-propylthiocarbamate(1−), $SCONR_2^-$. One of them, $NaHPd(SCONR_2)_4$, is unusual not only by its mode of formation but also by its structure.

Experimental Section

Analytical grade chemicals were used in all experiments. Carbonyl sulfide was made by dropwise addition of an aqueous NH_4SCN solution to aqueous H_2SO_4.

Potassium *N*,*N*-Di-*n*-propylthiocarbamate, $K(SCONR_2)$. Carbonyl sulfide was bubbled through a benzene solution of dipropylamine.[9] The salt $(R_2NH_2)(SCONR_2)$ was treated with KOH/EtOH for conversion to the potassium salt.

Bis(*μ*-*N*,*N*-di-*n*-propylthiocarbamato-*S*)bis(*N*,*N*-di-*n*-propylthiocarbamato-*O*,*S*)dipalladium(II), $Pd_2(SCONR_2)_4$ (A). To a suspension of 1.0 g (5.6 mmol) of $PdCl_2$ in 100 mL of concentrated aqueous NaCl was added 2.23 g (11.2 mmol) of $K(SCONR_2)$ dissolved in 10 mL of water. The mixture was stirred for 10 min and then extracted with chloroform. The organic layer was dried over $MgSO_4$ and concentrated. The oily product gave red crystals of A from acetonitrile; mp 96–98 °C dec. Yield: 2.1 g (87%).

Anal. Calcd for $C_{28}H_{56}N_4O_4Pd_2S_2$ (M_r = 853.8): C, 39.39; H, 6.61; N, 6.56; S, 15.02. Found: C, 39.41; H, 6.49; N, 6.63; S, 15.09.

Sodium Hydrogen Tetrakis(*N*,*N*-di-*n*-propylthiocarbamato)palladate (II), $NaHPd(SCONR_2)_4$ (D). To a suspension of 1.0 g (5.6 mmol) of $PdCl_2$ in 100 mL of concentrated aqueous NaCl was added 11.2 g (56.0 mmol) of $K(SCONR_2)$ dissolved in water. The mixture was stirred for 10 min and extracted with 2 × 50 mL of chloroform. The oil that remained after evaporation of the solvent was treated with petroleum ether. Orange crystals were obtained; mp 238–240 °C dec. Yield: 2.6 g (61%).

Anal. Calcd for $C_{28}H_{57}N_4NaO_4PdS_4$ (M_r = 771.4): C, 43.59; H, 7.44; N, 7.26; S, 16.62. Found: C, 43.61; H, 7.50; N, 7.31; S, 16.44.

***trans*-Bis(di-*n*-propylamine)bis(*N*,*N*-di-*n*-propylthiocarbamato)palladium(II), *trans*-$Pd(SCONR_2)_2(NHR_2)_2$ (B). Procedure 1.** The mother liquor from the synthesis of $NaHPd(SCONR_2)_4$ was concentrated, and the precipitating solid was recrystallized from hot 2-propanol. Yellow crystals were obtained; mp 100–102 °C dec. Yield: 1.1 g (17.5% with respect to the amounts used in the synthesis of D).

Anal. Calcd for $C_{26}H_{58}N_4O_2PdS_2$ (M_r = 629.3): C, 49.62; H, 9.29; N, 8.90; S, 10.19. Found: C, 49.41; H, 9.25; N, 8.82; S, 10.09.

Procedure 2. A solution containing 2.0 g (20 mmol) of NHR_2 and 0.85 g (1.0 mmol) of A in 100 mL of benzene was refluxed for 10 min. Evaporation of the solvent under vacuum yielded 1.1 g (88%) of B.; Mp. 100–102 °C dec. This product was identical with the product of procedure 1 (IR, ^1H NMR).

Procedure 3. A solution containing 2.0 g (20 mmol) of NHR_2 and 0.77 g (1.0 mmol) of $NaHPd(SCONR_2)_4$ in 100 mL of $CHCl_3$ was refluxed for 10 min. Evaporation of the solvent under vacuum afforded 0.52 g (82%) of B.; mp 101–102 °C dec. This product was identical with the product of procedure 1 (IR, ^1H NMR).

***trans*-Bis(triphenylphosphine)bis(*N*,*N*-di-*n*-propylthiocarbamato)palladium(II), *trans*-$Pd(SCONR_2)_2(PPh_3)_2$ (C). Procedure 1.** A solution containing 2.6 g (10 mmol) of PPh_3 and 0.85 g (1.0 mmol) of A in 200 mL of benzene was evaporated under vacuum to yield 1.48 g (78%) of yellow crystals, which were recrystallized from benzene; mp 196–198 °C.

Anal. Calcd for $C_{50}H_{58}N_2O_2P_2PdS_2$ (M_r = 951.5): C, 63.11; H, 6.14; N, 2.94; S, 6.74. Found: C, 63.36; H, 6.17; N, 2.88; S, 6.63.

Procedure 2. A solution containing 2.6 g (10 mmol) of PPh_3 and 0.77 g (1.0 mmol) of $NaHPd(SCONR_2)_4$ in 200 mL of benzene was briefly warmed to reflux temperature, and then the solvent was evaporated

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(1) Coucouvanis, D., Lippard, S. J., Eds. *Progress in Inorganic* Chemistry; Wiley: New York, 1979; Vol. 26, p 301.
(2) Burns, R. P.; McCullough, F. P.; McAuliffe, C. A. In *Advances in Inorganic Chemistry and Radiochemistry*; Emelēus, H. J., Sharpe, A. G., Eds.; Academic: New York, 1980; Vol. 23, p 211.
(3) McCormick, B. J.; Bereman, R.; Baird, D. *Coord. Chem. Rev.* **1984**, *54*, 99.
(4) Springsteen, K. R. M.; Greene, D. L.; McCormick, B. J. *Inorg. Chim. Acta* **1977**, *23*, 13.
(5) Van der Linden, J. G. M.; Blommerde, W.; Dix, A. H.; Pijpers, F. W. *Inorg. Chim. Acta* **1977**, *24*, 261.
(6) McCormick, B. J.; Stormer, B. P. *Inorg. Chem.* **1972**, *11*, 729.
(7) Hoskins, B. F.; Pannan, C. D. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 229.
(8) Gupta, V. D.; Nöth, H.; Rattay, W. *J. Chem. Soc., Dalton Trans.*, in press.
(9) *Houben-Weyl: Methoden der Organischen Chemie*, 4th ed.; Thieme: Stuttgart, New York, 1984; p 297.

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Table I. Single-Crystal X-ray Crystallographic Data for Complexes B–D[a]

	B	C	D	
temp, °C	18[b]	18[b]	18[b]	−35[c]
formula	$C_{26}H_{58}N_4O_2PdS_2$	$C_{50}H_{58}N_2O_2P_2PdS_2$	$C_{28}H_{57}N_4NaO_4PdS_4$	
mol wt	570	951.5	771.4	
cryst size, mm	0.10 × 0.25 × 0.31	0.32 × 0.20 × 0.33		
habit of cryst	yellow platelets	yellow needles	orange platelets	
cryst system	triclinic	monoclinic	monoclinic	
a, Å	9.196 (7)	9.847 (2)	15.037 (4)	14.953 (3)
b, Å	9.982 (9)	20.454 (7)	15.330 (5)	15.244 (9)
c, Å	10.862 (10)	12.215 (3)	16.997 (4)	16.968 (4)
α, deg	86.79 (7)	90	90	90
β, deg	74.64 (7)	101.19 (2)	98.75 (2)	98.70 (2)
γ, deg	64.80 (7)	90	90	90
V, Å^3	868 (1)	2408	3872	3823 (1)
Z	1	2	4	4
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	
μ, cm^{-1}	6.67	5.66	7.24	7.33
max/min transmission	0.829/0.754	0.825/0.790	0.627/0.610	
d_r, g/cm^3	1.095	1.312	1.323	1.340
scan range, deg	1	1	1.2	1.2
scan speed, deg/min	4–29.3	2–29.3	2–29.3	1.6
2θ range, deg	2–50	3–50	2–50	2–40
recipr space	$\pm h,\pm k,\pm l$	$h,k,\pm l$	$h,\pm k,\pm l$	$\pm h,k,\pm l$
no. of reflcns measd	5030	4667	8765	7505
no. of unique reflcns obsd	2749	3098	4790	3657
R(merge) with $I > n\sigma(I)$	2	3	3	1
no. of params refined	163	343	430	358
mean Δ/σ	0.019	0.198	0.26	<0.04
largest electron dens, e/Å^3	1	0.41	0.92	0.58
resid *R*[d]	0.070	0.047	0.079	0.053
resid R_w[e]	0.059	0.049	0.072	0.055
g[f]	0.0003	0.0047	0.000 26	0.0003

[a] A Syntex R3 automated four-circle X-ray diffractometer was used for crystallographic work and data collection at 18 °C, and an Enraf-Nonius CAD4 diffractometer for the low-temperature work (−35 ± 1 °C). Graphite-monochromatized Mo Kα radiation was used (λ = 0.710 69 Å), and crystals were sealed in glas capillaries. [b] Syntex R3 four-circle automated diffractometer. [c] Enraf-Nonius CAD4 diffractometer. [d] $R = \sum(|\Delta F|)/\sum(|F_o|)$; the function $\sum w(|F_o| - |F_c|)^2$ is minimized. [e] $R_w = \sum(w^{1/2}|\Delta F|)/\sum(w^{1/2}|F_o|)$. [f] $w = 1/[\sigma^2(F) + |g|F^2]$.

without further heating, under vacuum, to give 0.78 g (82%) of yellow material, which was recrystallized from benzene; mp 196–198 °C dec. This product was identical with the product of procedure 1 for C (IR, ^{1}H NMR).

Procedure 3. A solution containing 2.6 g (10 mmol) of PPh_3 and 0.63 g (1.0 mmol) of B in 200 mL of benzene was refluxed for 10 min. Evaporation of the solvent afforded 0.72 g (76%) of yellow material, which, after recrystallization from benzene, proved to be identical with the product of procedure 1 for C (IR, ^{1}H NMR); mp 196–199 °C dec.

All the new complexes are soluble in common organic solvents (benzene, alcohols, chloroform) and are practically insoluble in water.

Crystal Structure Determinations. Calculations were performed by employing the SHELXTL program package except for the low-temperature data set, where calculations were performed with the STRUX II program. Neutral-atom form factors, as supplied in the *International Tables for X-Ray Crystallography*, were used with anomalous dispersion corrections. The intensities of the data were corrected for changes in the intensities of 2 check reflections, measured after every 48 data. Lp correction as well as empirical absorption correction was applied for compounds B and C. The structures were solved by the Patterson method, followed by successive difference Fourier synthesis. Non-hydrogen atoms were refined with isotropic and anisotropic temperature factors. Many hydrogen atom positions were revealed, but calculated positions were used in the final refinements.

Crystallographic data are summarized in Table I, and atomic coordinates, in Tables II–IV.

Complex B. Carbon atoms C(11)–C(13) show anomalous bond lengths due to disorder. Therefore, high (>1 e/Å^3) residual electron density is found near these atoms, particularly C(12). Since a split-atom procedure did not greatly improve the result, the final calculation used the positions with the highest electron density. Except for the nitrogen-bonded hydrogen atoms, all other H positions were included in the refinement as rigid groups with their temperature factor parameter fixed to 1.2 times those of the respective carbon atom.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Compound B

atom	*x*	*y*	*z*	*U*[a]
Pd	5000	10 000	0	47 (1)
P	5355 (1)	10 689 (1)	1551 (1)	48 (1)
S	4574 (1)	9 194 (1)	1243 (1)	57 (1)
O	2112 (3)	9 256 (2)	−98 (3)	65 (1)
N	2292 (4)	8 507 (2)	1272 (3)	63 (2)
C(1)	2822 (4)	8 988 (2)	716 (4)	53 (2)
C(2)	868 (5)	8 285 (3)	847 (4)	80 (2)
C(4)	−1679 (6)	8 378 (4)	839 (6)	120 (3)
C(3)	−200 (6)	8 684 (3)	1240 (5)	100 (3)
C(5)	3033 (6)	8 209 (3)	2281 (5)	90 (3)
C(6)	2863 (9)	8 589 (5)	3362 (6)	145 (4)
C(7)	3590 (13)	8 343 (6)	4329 (8)	240 (8)
C(10)	3757 (4)	10 870 (2)	2050 (3)	50 (2)
C(11)	2517 (4)	10 587 (2)	1535 (4)	61 (2)
C(12)	1303 (5)	10 747 (3)	1898 (5)	77 (2)
C(13)	1331 (6)	11 165 (3)	2764 (5)	78 (2)
C(14)	2543 (6)	11 434 (3)	3280 (4)	72 (2)
C(15)	3756 (5)	11 298 (2)	2931 (4)	62 (2)
C(20)	6515 (4)	10 289 (2)	2702 (3)	47 (1)
C(21)	7802 (4)	10 093 (2)	2534 (4)	61 (2)
C(22)	8713 (5)	9 778 (3)	3370 (4)	69 (2)
C(23)	8357 (5)	9 653 (3)	4370 (4)	67 (2)
C(24)	7084 (6)	9 837 (3)	4547 (4)	84 (2)
C(25)	6155 (5)	10 144 (3)	3716 (4)	71 (2)
C(30)	6074 (4)	11 514 (2)	1500 (4)	51 (2)
C(31)	5328 (5)	11 967 (3)	797 (4)	69 (2)
C(32)	5841 (7)	12 600 (3)	733 (5)	90 (3)
C(33)	7089 (7)	12 776 (3)	1346 (6)	91 (3)
C(34)	7836 (6)	12 324 (3)	2051 (5)	90 (3)
C(35)	7328 (5)	11 704 (2)	2129 (4)	69 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Complex C. Carbon chain C(5)–C(7) shows comparatively large temperature factors indicating disorder, especially for C(7). Therefore, deviations from standard bond lengths result: N–C(5) = 1.440 Å, C(5)–C(6) = 1.569 Å, C(6)–C(7) = 1.353 Å. The same holds also for C(2) to C(4) with C(2)–C(3) being too short (1.480 Å) and C(3)–C(4) (1.572 Å) too long. The positions for the hydrogen atoms on C(5) to C(7) were not refined. U_i of all hydrogen atoms were fixed to approximately 1.2 times that of the respective carbon atom.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for Compound C

atom	*x*	*y*	*z*	U^a
Pd	0	0	0	43 (1)
S	−767 (2)	985 (3)	2120 (2)	77 (1)
O	2001 (7)	1378 (8)	1748 (5)	93 (3)
N(1)	349 (8)	1978 (8)	3753 (6)	76 (3)
N(2)	2174 (7)	353 (6)	−590 (5)	55 (2)
C(1)	694 (8)	1471 (8)	2533 (6)	58 (3)
C(11)	1487 (14)	2648 (11)	4026 (9)	88 (5)
C(12)	2807 (16)	1433 (11)	4382 (10)	112 (7)
C(13)	4022 (12)	2167 (12)	4654 (10)	101 (5)
C(14)	−1072 (12)	2001 (10)	4830 (8)	89 (5)
C(15)	−2398 (16)	3458 (13)	5173 (12)	132 (8)
C(16)	−3702 (14)	3513 (14)	6463 (10)	116 (7)
C(21)	3777 (8)	−1008 (8)	−967 (6)	62 (3)
C(22)	4016 (10)	−2138 (9)	65 (8)	81 (4)
C(23)	5698 (10)	−3457 (10)	−307 (10)	97 (5)
C(24)	2114 (8)	1508 (8)	−1532 (6)	61 (3)
C(25)	617 (11)	2967 (9)	−1123 (7)	80 (4)
C(26)	652 (14)	4176 (10)	−2032 (9)	102 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Atomic Coordinates and Isotropic Thermal Parameters ($Å^2 \times 10^2$) for Compound D

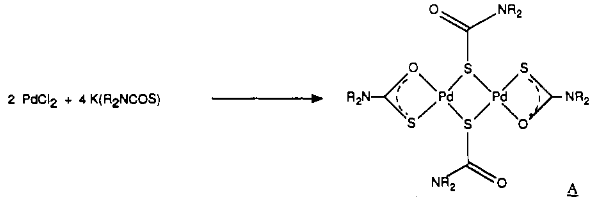
atom	*x*	*y*	*z*	U^a
Pd	0.11709 (4)	0.15588 (4)	0.11276 (4)	3.97 (1)
S(1)	0.0762 (2)	0.1564 (2)	0.2401 (1)	5.18 (5)
S(2)	0.1778 (1)	0.1652 (2)	−0.0055 (1)	5.28 (5)
S(3)	−0.0193 (1)	0.2234 (1)	0.0626 (1)	4.72 (5)
S(4)	0.2531 (1)	0.0887 (1)	0.1689 (1)	4.89 (5)
Na	0.0138 (2)	−0.0215 (2)	0.0950 (1)	2.81 (5)
O(1)	−0.0462 (3)	0.0399 (3)	0.1773 (3)	4.5 (1)
O(2)	0.0341 (4)	0.1396 (3)	−0.1146 (3)	5.0 (1)
O(3)	−0.0580 (3)	0.0609 (3)	0.0120 (3)	3.5 (1)
O(4)	0.1317 (3)	−0.0395 (3)	0.1629 (3)	4.4 (1)
N(1)	−0.0718 (5)	0.0986 (6)	0.2920 (4)	8.2 (2)
N(2)	0.0919 (5)	0.2742 (4)	−0.1179 (4)	5.2 (2)
N(3)	−0.1788 (4)	0.1503 (4)	0.0150 (4)	4.3 (1)
N(4)	0.2624 (4)	−0.0672 (4)	0.2429 (4)	4.7 (2)
C(1)	−0.0212 (5)	0.0920 (6)	0.2338 (5)	5.0 (2)
C(2)	0.0915 (5)	0.1943 (5)	−0.0849 (5)	4.5 (2)
C(3)	−0.0903 (5)	0.1363 (5)	0.0266 (4)	3.9 (2)
C(4)	0.2094 (5)	−0.0131 (5)	0.1921 (4)	4.5 (2)
C(11)	−0.1558 (7)	0.0466 (8)	0.2865 (6)	8.4 (3)
C(12)	−0.1410 (8)	−0.045 (1)	0.3120 (8)	10.9 (4)
C(13)	−0.227 (1)	−0.097 (1)	0.298 (1)	13.7 (5)
C(14a)	−0.067	0.185	0.348	7.3 (5)*
C(14b)	−0.035	0.136	0.375	8.8 (6)*
C(15a)	−0.028	0.144	0.421	11.5 (8)*
C(15b)	−0.097	0.226	0.360	11.5 (8)*
C(16a)	−0.013	0.230	0.481	11.3 (8)*
C(16b)	−0.055	0.268	0.448	14 (1)*
C(21)	0.0275 (7)	0.2946 (6)	−0.1893 (6)	6.6 (3)
C(22)	0.0736 (9)	0.3024 (9)	−0.2647 (6)	10.0 (4)
C(23)	0.014 (1)	0.327 (1)	−0.3348 (8)	12.0 (4)
C(24)	0.1492 (7)	0.3464 (6)	−0.0848 (6)	6.9 (2)
C(25)	0.0983 (9)	0.4085 (7)	−0.0338 (7)	9.6 (3)
C(26)	0.150 (1)	0.4910 (9)	−0.0150 (9)	13.1 (5)
C(31)	−0.2208 (6)	0.2361 (6)	0.0261 (6)	6.4 (2)
C(32)	−0.2545 (8)	0.2825 (7)	−0.0503 (8)	9.2 (3)
C(33)	−0.187 (1)	0.3037 (8)	−0.0994 (8)	13.3 (5)
C(34)	−0.2427 (5)	0.0784 (6)	−0.0099 (5)	5.1 (2)
C(35)	−0.2879 (6)	0.0441 (7)	0.0601 (7)	7.8 (3)
C(36)	−0.3685 (7)	−0.009 (1)	0.0319 (8)	10.3 (4)
C(41)	0.2279 (6)	−0.1521 (6)	0.2656 (5)	6.2 (2)
C(42)	0.2010 (7)	−0.1519 (7)	0.3479 (6)	7.8 (3)
C(43)	0.1277 (8)	−0.0873 (9)	0.3571 (7)	9.5 (3)
C(44)	0.3566 (6)	−0.0467 (6)	0.2758 (5)	5.6 (2)
C(45)	0.4243 (6)	−0.0813 (6)	0.2235 (6)	6.9 (3)
C(46)	0.5195 (7)	−0.0755 (7)	0.2634 (7)	8.3 (3)

[a] Asterisk indicates equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Complex D: Low Temperature. Disorder was found at the carbon chain C(14)–C(16) bound to the N(1) atom. Forty-nine H atoms were given isotropic U_i, and eight H atoms were not taken into account in the final refinement. Positions and U_i of the H atoms were not refined in the final steps. Seven of the eight hydrogen atoms not taken into account were those at the disordered propyl group; the eighth is the "acidic" proton. It should be noted that in the final refinement only the positions of the disordered propyl group, not their *U* parameters, were included.

Results and Discussion

Syntheses and Transformations of R_2NCOS–Pd(II) Complexes. If $PdCl_2$ and $K(SCONR_2)$ are reacted in aqueous NaCl at a mole ratio of 1:2, $Pd_2(SCONR_2)_4$ (A) is formed according to eq 1. Its structure has been deduced from IR and NMR data (v.i.). However, IR data indicate that the dimer is not the only species present, and this will be discussed later. The suggested structure for compound A is supported by its ready conversion into $Pd(SCONR_2)_2(L)_2$ ($L = NHR_2, PPh_3$) on adding dipropylamine or triphenylphosphine to solutions of A as described by eq 2 and 3. As will be demonstrated, complexes B and C are both present as the trans isomers.



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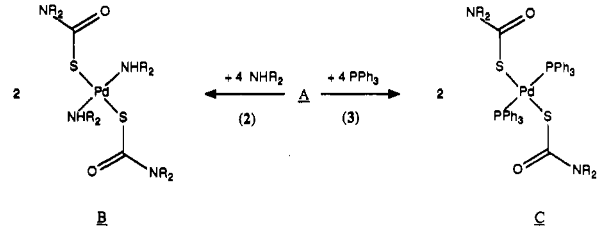

If the reaction between $PdCl_2$ and $K(SCONR_2)$ is carried out in aqueous NaCl solution at a mole ratio of 1:10, then four R_2NCOS ligands are bonded to the palladium center. The reaction can be described as shown in eq 4. Thus, if a sufficient amount of R_2NCOS^- anion is available, a 1:4 metal to ligand stoichiometry is energetically more favorable than the 1:2 ratio, which can only be enforced by creating a ligand deficiency.

$$PdCl_2 + 2\ NaCl + 4\ K(R_2NCOS) + H_2O \longrightarrow \underset{\underline{D}}{NaHPd(SCONR_2)_4} + 4\ KCl + NaOH \qquad (4)$$

Upon heating of the sodium salt (crystallization from hot 2-propanol), an interesting novel transformation occurs in which two of the four R_2NCOS ligands lose COS, resulting in the formation of compound B as depicted in eq 5. This dipropylamine complex can also be obtained by treating $NaHPd(SCONR_2)_4$ with an excess of NHR_2 in hot benzene or $CHCl_3$.

$$\underline{B} \xrightarrow[\substack{-\ 2\,NHR_2 \\ (6)}]{+\ 2\,PPh_3} \underline{C} \xleftarrow[\substack{-\ NaSCONR_2 \\ -\ NHR_2,\ -\ COS \quad (5)}]{+\ 2\,PPh_3} \underline{D} \qquad (5)$$

Addition of an excess of triphenylphosphine to solutions of the palladium complexes B and D affords *trans*-bis(triphenylphosphine)bis(*N*,*N*-di-*n*-propylthiocarbamato)palladium(II) according to eq 6. These observations suggest increasingly stronger bonding in the series of ligands $NHR_2 < SCONR_2^- < PPh_3$.

Infrared Spectra. Prior to this work, the structures of the few known (thiocarbamato)palladium complexes have been deduced solely from infrared and ^{13}C NMR data, which are also widely used techniques for elucidating the structures of mtc and dtc complexes of other metals.[1-3] With the use of the X-ray structures

Table V. Infrared Data and Bonding Modes for the Palladium Dipropylthiocarbamato Complexes

compd	wavenumber, cm^{-1}	C–N, Å	SCONR$_2$ bonding
A	1640 s		S-bridging
	1612 m		monodentate;
	1582 s		S,O-bidentate
	1560 m		
B[a]	1564 w		
	1530 vs		
C	1587 m	1.355	S-bonded
	1578 vs		monodentate
	1570 s		
D	1562 m	1.320	S-bonded
	1535 vs	1.335	monodentate

[a] Weak N–H stretching band observed at 3060 cm^{-1} (H bond to the C=O group).

reported in this work, it is possible to check and substantiate the assignments and interpretation of the major IR bands of mtc complexes.

N,N-Dialkylthiocarbamate esters have ν(C=O) stretching bands between 1640 and 1670 cm^{-1}. Upon complex formation involving the C(O)S$^-$ group, this band is replaced by an intense absorption in the 1500–1590-cm^{-1} range, which is referred to by McCormick et al. as the ν(C$\cdots$N) band.[3] This band reflects the importance of the canonical form I in mtc ligands, involving restricted rotation about the C–N bond. According to Rao et al.[10] monodentate bonding of this ligand through sulfur would be associated with the appearance of ν(C=N) above 1545 cm^{-1}, whereas its location below 1545 cm^{-1} would indicate its bidentate character. Exceptions to this rule have been noted.[11] In a molybdenum *N,N*-dimethyldithiocarbamate mixed-ligand complex, a 1530-cm^{-1} band has been assigned to a vibration of the NCS moiety.[12] The exact origin of the bands at 1500–1590 cm^{-1} apparently involves uncertainties and requires further study using labeled compounds.

The IR bands observed between 1500 and 1700 cm^{-1} in the present study are listed in Table V. Compound A reveals four bands in this region. The high-frequency bands can be assigned to bridging mtc ligands. These correspond with a band around 1650 cm^{-1}, which has been observed by Van der Linden et al.[5] for dinuclear complexes Pd$_2$(mtc)$_2$(Ph$_2$dtc)$_2$, assigned to mtc ligands coordinated through a bridging sulfur atom between two Pd atoms. The same assignment was made[13] for the dinuclear S-bridged complex Rh$_2$(mtc)$_2$(CO)$_4$, having an IR band at 1660 cm^{-1}. It seems that a band above 1600 cm^{-1} in mtc complexes points to the presence of a bridging sulfur atom.

It has been frequently observed that the relative intensity of the double bands above and below 1600 cm^{-1} in compound A varies with preparation conditions, indicating that we may be having a mixture of several oligomeric species. Such a possibility has already been mentioned by Van der Linden and co-workers,[5] who reported bands at 1570, 1580, 1620, and 1635 cm^{-1} for bis(piperidinecarbothioato)palladium, a red polymeric product. In the present case, bands between 1535 and 1587 cm^{-1} can be observed for compounds B–D, although the monodentate bonding of the R$_2$NCOS ligand is demonstrated by the X-ray structures. It appears, therefore, that IR data are inconclusive concerning the bonding mode (monodentate vs bidentate). The bands at 1500–1590 cm^{-1} in such complexes may be coupled ν(C$\cdots$O + C$\cdots$N) modes.

^{13}C NMR Spectra. The chemical shifts for the complexes synthesized are listed in Table VI. The poorly resolved resonances observed in the ^{13}C NMR spectrum of A do not offer much information about its structure. The broad singlets may be due to some exchange or dissociation–association process, which has not been studied in any detail.

Table VI. ^{13}C NMR Chemical Shifts[a] (ppm, Relative to TMS) of Complexes A–D

compd	C(1)	C(2)	C(3)	C(4)	arom ring
A	177.8	53.5 b	22.2 b	11.5	
	163.5 b	52.7 b	20.8 b		
	162.2 b	49.8 b			
B	178.3	54.7	22.5	11.7	
		51.6	21.6	11.4	
		48.6			
C	174.1	50.6 b	21.6	11.3	135.2
					132.7
					128.4
					127.5
D	187.4	53.8	21.6–20.8[c]	12.0	
	182.0	52.9		11.7–11.4[c]	
	181.5	52.6			
	181.0	50.3			
		49.6			
		48.2			
		48.1			

[a] All spectra were recorded in CDCl$_3$ at room temperature; b = broad. [b] Carbon label key: [(C(4)H$_3$–C(3)H$_2$–C(2)H$_2$)$_2$N–C(1)(O)-S$^-$]. [c] Not completely resolved.

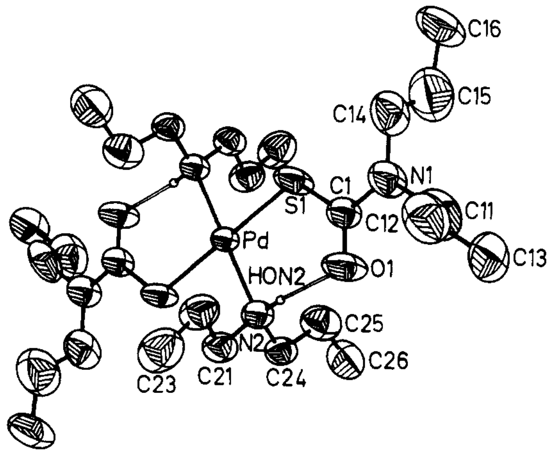

Figure 1. ORTEP plot of compound B. Thermal ellipsoids represent a 50% probability.

The spectrum of D reveals four different carbonyl carbons; it also shows three pairs of lines in the C(3) carbon range (~50 ppm). This is consistent with its X-ray structure: there are four types of bonded R$_2$NCOS ligands.

Compound B shows only one sharp singlet for C(1), in accord with the X-ray structure. C(2) and C(3) of the propyl group in the NHR$_2$ ligands appear at 54.7 and 22.5 ppm, respectively. The resonances at 51.6 and 48.6 ppm indicate the nonequivalence of C(2) atoms in the R$_2$NCOS ligands resulting from the marked double-bond character of its C–N bond.

A simple situation emerges for compound C, singlets being observed for all types of R$_2$NCOS carbons. The single broad resonance of the C(2) atoms indicates no hindrance of rotation around the C(1)–N bond at ambient temperature in this complex.

X-ray Structures. Since IR and NMR data alone were insufficient to reliably characterize the structure of the complexes A–D, X-ray diffractometry was used on compounds B–D for which single crystals were available. Selected bonding parameters are summarized in Table VII, and Figures 1–3 show plots of the molecular structures.

Complexes B–D crystallize in centrosymmetric space groups. In the case of B and C the Pd atoms occupy a center of inversion. Therefore, the configurations represent the trans isomers of square-planar Pd(II) complexes.

The di-*n*-propylthiocarbamate groups in B and C act as monodentate ligands with the sulfur atom bonded to palladium, as

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(10) Crosby, A. B.; Magee R. J.; O'Connor, M. J.; Tantry, K. N.; Rao, C. N. R. *Proc. Indian Acad. Sci., Sect. A* **1979**, *88*, 393.

(11) Pierpont, C. G.; Dickinson, R. C.; McCormick, B. J. *Inorg. Chem.* **1974**, *13*, 1674.

(12) Brunner, H.; Wachter, J. *J. Organomet. Chem.* **1979**, *175*, 285.

(13) Krankovits, E. M.; Magee, R. J.; O'Connor, M. J. *Inorg. Chim. Acta* **1973**, *7*, 528.

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes B–D (Estimated Standard Deviations in Parentheses)

	B	C	D, −35 °C	D, 18 °C		B	C	D, −35 °C	D, 18 °C
Pd–S(1)	2.361 (4)	2.332 (2)	2.333 (1)	2.331 (3)	C(1)–O(1)	1.247 (8)	1.228 (5)	1.257 (6)	1.247 (9)
Pd–S(2)			2.329 (1)	2.325 (3)	C(2)–O(2)			1.248 (5)	1.245 (9)
Pd–S(3)			2.327 (1)	2.321 (3)	C(3)–O(3)			1.286 (5)	1.281 (8)
Pd–S(4)			2.347 (1)	2.344 (3)	C(4)–O(4)			1.259 (5)	1.262 (8)
Pd–N(2)/P	2.107 (6)	2.331 (2)			Na–O(1)			2.003 (3)	1.992 (5)
S(1)–C(1)	1.760 (8)	1.770 (4)	1.746 (5)	1.752 (9)	Na–O(2)			1.983 (3)	1.981 (5)
S(2)–C(2)			1.775 (5)	1.769 (7)	Na–O(3)			2.064 (3)	2.062 (5)
S(3)–C(3)			1.751 (5)	1.735 (7)	Na–O(4)			1.973 (3)	1.976 (5)
S(4)–C(4)			1.751 (5)	1.732 (8)	Na′–O(3)			2.111 (3)	2.117 (5)
N(1)–C(1)	1.352 (8)	1.355 (6)	1.336 (6)	1.335 (12)	Na–Na′			3.255 (3)	3.259 (5)
N(2)–C(2)			1.342 (6)	1.320 (9)	Pd–Na			3.106 (1)	3.101 (3)
N(3)–C(3)			1.326 (5)	1.340 (9)					
N(4)–C(4)			1.358 (6)	1.354 (9)					

	B	C		D, −35 °C	D, 18 °C
S–Pd–N(2)/P	95.3 (2)	85.2 (1)	S(1)–Pd–S(3)	89.99 (5)	90.0 (1)
P/N(2)–Pd–S′	84.7 (2)	94.8 (1)	S(2)–Pd–S(3)	95.27 (5)	95.3 (1)
Pd–S–C(1)	115.4 (2)	102.5 (2)	S(1)–Pd–S(4)	87.57 (5)	87.5 (1)
S–C(1)–N(1)	117.4 (5)	115.6 (3)	S(2)–Pd–S(4)	87.11 (5)	87.2 (1)
S–C(1)–O	123.7 (5)	123.4 (4)	S(3)–Pd–S(4)	177.53 (5)	177.5 (1)
N(1)–C(1)–O	118.9 (7)	121.0 (4)	S(1)–Pd–S(2)	171.46 (5)	171.5 (1)

	D, −35 °C	D, 18 °C		D, −35 °C	D, 18 °C
Pd–S(1)–C(1)	105.9 (2)	105.7 (2)	Pd–Na–O(3′)	96.62 (9)	96.6 (1)
Pd–S(2)–C(2)	109.6 (2)	109.8 (3)	O(1)–Na–O(3)	87.1 (1)	87.6 (2)
Pd–S(3)–C(3)	104.1 (2)	104.1 (2)	O(1)–Na–O(4)	96.5 (1)	96.2 (1)
Pd–S(4)–C(4)	98.6 (2)	98.9 (3)	O(3)–Na–O(4)	144.1 (1)	143.7 (2)
S(1)–C(1)–O(1)	123.4 (4)	123.4 (6)	O(1)–Na–O(2′)	95.5 (1)	95.5 (2)
S(2)–C(2)–O(2)	121.0 (4)	121.2 (5)	O(3)–Na–O(2′)	120.2 (1)	119.9 (2)
S(3)–C(3)–O(3)	121.3 (3)	122.3 (5)	O(4)–Na–O(2′)	95.1 (1)	95.8 (2)
S(4)–C(4)–O(4)	123.2 (4)	122.9 (5)	O(1)–Na–O(3′)	164.6 (1)	165.1 (2)
Pd–Na–O(1)	78.1 (1)	78.2 (2)	O(3)–Na–O(3′)	77.5 (1)	77.5 (2)
Pd–Na–O(2)	163.9 (1)	164.1 (2)	O(4)–Na–O(3′)	95.4 (1)	95.2 (2)
Pd–Na–O(3)	74.69 (9)	74.8 (1)	O(2′)–Na–O(3′)	93.1 (1)	92.9 (2)
Pd–Na–O(4)	71.2 (1)	70.8 (2)	∑ at N(1)	355.7	358.1

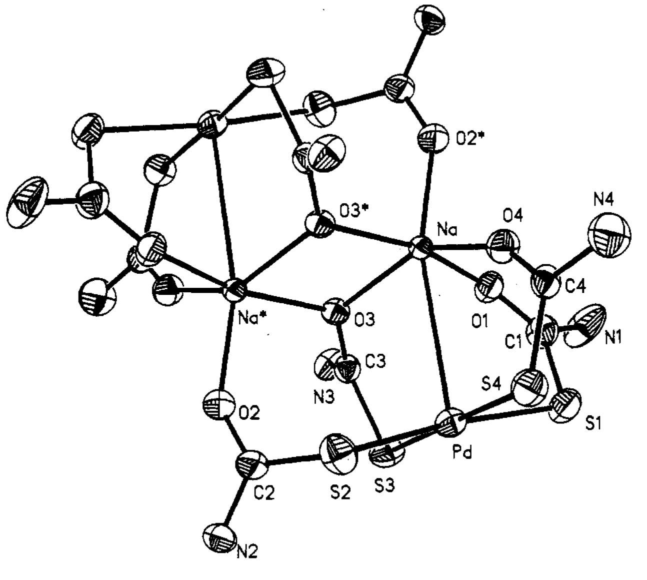


Figure 2. ORTEP plot of $NaHPdL_4$ (compound D). The propyl groups have been omitted in order to present a clear picture of the inner core of this molecule.

expected for a preferred interaction of the soft side of the ligand with a soft metal.

The striking feature of $Pd(SCONR_2)_2(NHR_2)_2$ is the almost perfect plane PdS(1)C(1)O(1)N(2)H including the hydrogen atoms of the dipropylamine ligands, which form hydrogen bonds to the carbonyl oxygen atoms. Among the three complexes investigated, $Pd(SCONR_2)_2(NHR_2)_2$ contains the longest Pd–S bond. This probably reflects the strong σ-donor character of the amine nitrogen atom N(2). In contrast, the Pd–S and Pd–P bonds of the triphenylphosphine complex C are identical in length in spite of the somewhat larger atomic radius of the phosphorus as compared to that of the sulfur atom. This can be taken as a result of the trans-effect of the phosphine ligand. The larger bulk of the PPh_3 unit in C as compared to that of the amine ligand in B has almost no influence on the bond angles at the Pd atom. However, it influences strongly the orientation of the SCON plane of the monothiocarbamate ligand. This plane is approaching an orthogonal orientation (72°) with respect to the PdP_2S_2 plane,

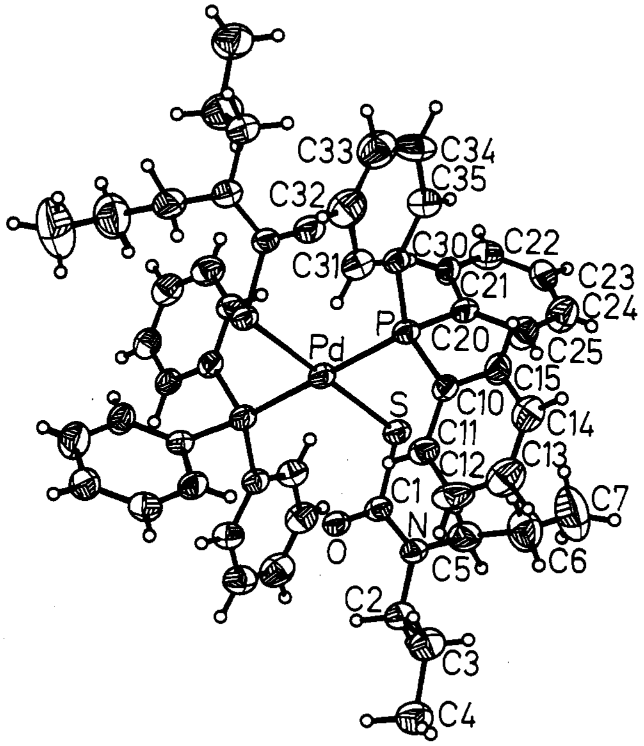


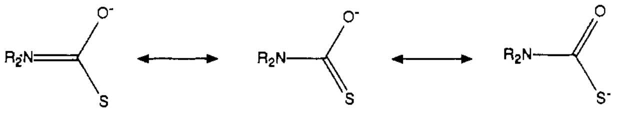
Figure 3. ORTEP plot of complex C. Thermal ellipsoids represent a 30% probability.

thus reducing steric interaction with the PPh_3 ligands. Also, the C(2)NC(5) plane of the ligand R_2NCOS is only slightly twisted (12°) out of the N(1)C(1)O(1)S(1) plane, allowing a still excellent delocalization of negative charge. A comparison of the ligand parameters for B and C shows a significant difference only in the C–O bond lengths. This bond is definitely longer in B than in C, a further consequence of the hydrogen bridge bond in the former. This bonding influences also the bond angle at S in B, which is almost 13° wider than that in the phosphine complex.

The complex $NaHPd(SCONR_2)_4$ (D) is interesting for a number of reasons. The most striking aspect is displayed in Figure 2 showing that it is in fact a dimeric molecule. For reasons outlined later, two sets of data were recorded for D, one at 18 °C and one at −35 °C. Since the low-temperature data are more accurate, we shall refer to these in the discussion.

The structure of D also has a center of symmetry located at the center of the NaO(3)Na′O(3′) four-membered ring. Each Pd atom of the dimer is surrounded by four sulfur atoms in an almost square-planar arrangement. The average Pd–S bond length is 2.334 Å, but one out of the four Pd–S bonds, Pd–S(4), is longer although still shorter than the Pd–S bonds in B. There is no obvious reason for the elongation of this specific Pd–S bond. Considering the structure of the sodium salt, one could imagine that the Pd–S(2) bond is unique because the oxygen atom of this R_2NCOS group binds the two sodium atoms. This, however, is not the case, but the unique feature of this R_2NCOS group is reflected in the larger S(2)–Pd–S(3) bond angle (95.3°), while all other S–Pd–S bond angles are smaller than 90°, and this is obviously the consequence of steric interactions.

All four thiocarbamate ligands in $NaHPd(SCONR_2)_4$ act as COS bridging ligands between the Pd atom and sodium atom. The C(1)O(1)S(1) and the C(4)O(4)S(4) ligands have equivalent bonding functions bridging the Pd atom to the Na atom. The fragment C(2)O(2)S(2) binds the palladium atom and the symmetry-related Na atom, and the fragment C(3)O(3)S(3) bind to the Pd atom but its oxygen shows μ_2 function by bridging the two sodium atoms. As a consequence, one might expect that the structural features of the three nonequivalent ligands will be different. Actually, the N(3)C(3)O(3)S(3) ligand contains the longest C–O and the shortest C–N bond. Therefore, the resonance contribution II adds strongly to the ground state of this ligand.



I II III

On the other hand, a relatively long C–N bond is found for the unit C(4)N(4)O(4)S(4), in addition to a longer C–O bond, and this implies that resonance form III has more weight for this group. All the data suggest similar but slightly different bonding situations for all four ligands, and this is reflected in their ^{13}C NMR spectra because C(4) and C(1) have different chemical environments.

Finally, the sodium atoms in complex D can be considered as hexacoordinated. Each sodium atom is surrounded by five oxygen atoms at distances ranging from 2.111 to 1.973 Å, the longest bond resulting from the oxygen atoms O(3) and O(4). The oxygen polyhedron has the form of a distorted tetragonal pyramid with the sodium atom sitting above the tetragonal plane. While the O(2)–Na–O(1) and O(2)–Na–O(4) bond angles are equal, and O(2)–Na–O(3′) is only 3° smaller, a rather large O(2)–Na–O(3) bond angle (119.9°) is observed, which is more than 20° wider than any of those so far discussed. There is also an uneven distribution of O–Na–O bond angles in the "plane" of the tetragonal pyramid, the smallest (O(3)–Na–O(3′)) being 77.5° for the four-membered ring and the largest (96.2°) opposite to the ring. However, the sum of the bond angles is 356.5°, thus approaching the 360° for a perfect plane quite closely. This NaO_5 polyhedron is completed to a distorted octahedron if a Na–Pd interaction is taken into consideration. The distance between these two atoms amounts to 3.106 Å, which is shorter than the Na–Na′ distance (3.255 Å) of the four-membered ring. Probably, one would not consider this Na–Pd distance as a metal–metal bond. However, similar distances have also been observed in various intermetallic phases.[14] Thus, the sodium ions are trapped in a cavity of oxygen atoms reminiscent of clathrates, and this also explains the solubility of D in organic nonpolar solvents.

The stoichiometry of compound D requires an acidic proton. This proton could not be located in the crystal structure analysis. We therefore assume that it is either O- or N-bonded. Since there are four nitrogen atom sites per acidic proton in D, the electron density resulting from this unique proton by an even distribution over these sites will not allow its unambiguous detection. However, a good guess can be made by comparing the data obtained at 18 °C with those at −35 °C. The bond angles at the nitrogen atoms in the room-temperature structure show that these possess almost perfect trigonal-planar geometry. Only N(1) deviates more than average from planarity by being slightly pyramidal. This pyramidalization increases at lower temperature. We, therefore, assume that the unique hydrogen atom will bind to the N(1) atom at low temperature, while not being localized at ambient temperature. If it does bind to a single site, a change in the overall symmetry will occur, and this could also lead to a change in the crystal symmetry. Indeed, if the orange crystals of D are cooled below −45 °C, they suddenly become turbid and then burst to produce a yellow powder, we assume due to a structure change in the crystal.

Conclusions

The sulfur bridges in bis(di-*n*-propylthiocarbamato)palladium (A) can be cleaved by dipropylamine or triphenylphosphine, and the trans complexes B and C are obtained. They can also be broken by the ligand $R_2NC(O)S^-$; however, $NaHPd(SCONR_2)_4$ (D) is formed instead of $Na_2Pd(SCONR_2)_4$. D is dimeric; its $Pd(SCONR_2)_4$ units encapsulate unexpectedly the Na atoms via O coordination, explaining its solubility in organic solvents. This novel behavior suggests that monothiocarbamates may be useful for extraction processes.

Supplementary Material Available: Tables of all bonding parameters, anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, X-ray structure analysis details, and least-squares planes and stereoplots of the unit cell and core of complex D (32 pages); listings of observed and calculated structure factors (85 pages). Ordering information is given on any current masthead page.

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(14) Thronberens, W.; Sinnen, H. D.; Schuster, H.-V. *J. Less-Common Met.* **1980**, *76*, 99.