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Structure, Thermal Stability and Gas Chromatographic Behavior of Some Dialkyldithiocarbamate Chelates of Palladium(II)

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Four palladium(II) chelates with the dipropyldithiocarbamate (DPDTC), dibutyldithiocarbamate (DBDTC), di-isobutyldithiocarbamate (DIBDTC), and di(trifluoroethyl)dithiocarbamate (FDEDTC) ligands were crystallized and studied by X-ray diffraction techniques. The compounds form monoclinic crystals, space group is $P2_1/c$. The unit cell constants are a=8.388(1), b=17.992(2), c=14.204(2) Å, β=109.14(1)°; a=8.959(3), b=13.948(5), c=11.072(5) Å, β=113.16(3)°; a=11.890(9), b=13.210(4), c=16.549(9) Å, β=98.36(5)°; and a=8.537(3), b=8.874(3), c=13.119(6) Å, β=101.68(3)° for $Pd(DPDTC)_2$, $Pd(DBDTC)_2$, $Pd(DIBDTC)_2$, and $Pd(FDEDTC)_2$, respectively. The structures were refined to R values 0.033–0.059. In all cases the Pd(II) ion is coordinated by four S-atoms in a planar arrangement.

The infrared absorption frequencies were measured for these chelates as well as for the diethyl derivative (DEDTC) and correlated with the resonance forms and structures. Volatility trends observed in TG and DSC experiments were compared with capillary gas chromatographic behavior. Fluorination markedly increases the volatility and stability against thermal degradation. For the other chelates, no clear trends were observed in the TG/DSC data. The chromatographic elution order (DEDTC<DPDTC≃DIBDTC<DBDTC) indicates the effects of the molecular weight and the shape of the molecule.

Dialkyl-substituted dithiocarbamic acids have proved to be highly versatile chelating agents for the separation of metals as metal chelates by gas chromatography.[1] Their good performance in liquid–liquid extraction and other analytical procedures[2] makes them further attractive for the determination of metals by gas chromatography.

The most important requirements for successful chromatographic elution are volatility and thermal and solvolytic stability. From the available volatility data for metal dithiocarbamate chelates, it is difficult to recognize well-defined trends. No simple correlation has been found between the volatility and structure,[3] even though ligand structure appears to have a significant effect on both the thermal stability and volatility of many other metal chelates.[4–6]

Thus, Moshier and Sievers found that the replacement of hydrogen atoms by fluorine atoms in β-diketones results in a marked increase in the volatility of the metal chelates compared with that of the nonfluorinated analogs.[7] Tavlaridis and Neeb[8] showed recently that fluorination of diethyldithiocarbamate chelates also leads to a large increase in volatility. This increase occurs without change in thermal stability and with a rise in vapor pressure of the order of more than two decades.[9] For the time being di(trifluoroethyl)-dithiocarbamate seems to be one of the most useful ligands for the determination of trace elements as metal chelates by gas chromatography.[10]

In our laboratory (M.-L. R.) palladium chelates have been used as internal standards in gas chromatographic determinations of metals.[11] The purpose of the present work was to study the influence of the ligand structure on the thermal

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properties and gas chromatographic behavior of some palladium dialkyldithiocarbamate chelates having propyl, butyl, isobutyl, and trifluoroethyl as substituents.

EXPERIMENTAL

Preparation of palladium chelates. Bis(dipropyldithiocarbamato)palladium(II) and bis(dibutyldithiocarbamato)palladium(II), [Pd(DPDTC)$_2$ and Pd(DBDTC)$_2$], were prepared as previously described [12] and purified by recrystallization from chloroform–ethanol mixture (1:1, *v*:*v*).

Bis(di-isobutyldithiocarbamato)palladium(II), [Pd(DIBDTC)$_2$] was prepared by a method analogous to that used for Pd(DPDTC)$_2$ and Pd(DBDTC)$_2$. Pd(DIBDTC)$_2$ was recrystallized from acetone and ethanol–chloroform (1:1).

Bis[di(trifluoroethyl)dithiocarbamato]palladium(II), [Pd(FDEDTC)$_2$], was synthesized by mixing aqueous solutions of $PdCl_2$ (Merck) and sodium di(trifluoroethyl)dithiocarbamate.[9] The precipitate was recrystallized from acetone–chloroform (1:10). All palladium chelates formed yellow prismatic crystals.

X-ray crystallography. Data for Pd(DPDTC)$_2$ and Pd(DBDTC)$_2$ were collected at ambient temperature on a Syntex $P2_1$ diffractometer, and for Pd(DIBDTC)$_2$ and Pd(FDEDTC)$_2$ on a Nicolet R3 m diffractometer. Mo$K\alpha$ radiation (λ=0.71069 Å) with graphite monochromator was used. Accurate cell parameters were obtained for the four chelates from 20–24 centered reflections in the range $20° \leq 2\theta \leq 25°$ and are listed, along with other crystallographic data, in Table 1. Intensities were corrected for background, polarization and Lorentz factors. Empirical absorption corrections were made from ψ-scan data. Data collection was conducted according to standard procedures; data relevant to this phase of the work are also presented in Table 1. The structures were solved by the heavy atom method. In Pd(DPDTC)$_2$, Pd(DBDTC)$_2$, and Pd(FDEDTC)$_2$ the palladium atoms were located in special positions and in Pd(DIBDTC)$_2$ in the general positions. All other nonhydrogen atoms were found in successive Fourier maps with atomic scattering factors taken from refer-

Table 1. Crystallographic data.

Compound	Pd(DPDTC)$_2$	Pd(DBDTC)$_2$	Pd(DIBDTC)$_2$	Pd(FDEDTC)$_2$
Formula	$C_{14}H_{28}N_2S_4Pd$	$C_{18}H_{36}N_2S_4Pd$	$C_{18}H_{36}N_2S_4Pd$	$C_{10}H_8F_{12}N_2S_4Pd$
Molecular mass	459.1	515.2	515.2	618.9
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	8.388(1)	8.959(3)	11.890(9)	8.537(3)
b, Å	17.992(2)	13.948(5)	13.210(4)	8.874(3)
c, Å	14.204(2)	11.072(5)	16.549(9)	13.119(6)
β, deg	109.14(1)	113.16(3)	98.36(5)	101.68(3)
V, Å^3	2025.1(5)	1272.(1)	2572.(3)	973.2(7)
Z	4	2	4	2
μ(Mo$K\alpha$), cm^{-1}	12.9	10.4	10.2	14.7
Density, calc kg dm^{-3}	1.51	1.34	1.33	2.11
Range of transmission	0.894–0.722	0.856–0.798	0.861–0.701	0.499–0.422
Radiation used	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
Scan range, deg of 2θ	2–50	3–45	3–50	5–60
hkl range	−10, 0, 0 10, 22, 16	0, 0, −11 9, 16, 11	0, 0, −20 15, 16, 20	0, 0, −19 13, 13, 19
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
No. of refl. measured	3838	1479	4960	3171
No. of unique data[a]	2356	857	2629	2033
R_1[b]	0.042	0.046	0.059	0.033
R_2[c]	0.046	0.044	0.059	0.034
Goodness of fit[d]	2.03	1.29	1.92	1.11

[a] $|F| > 5\sigma(|F|)$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] Weight $= 1/(\sigma^2|F| + 0.005\ F^2)$ [d] Goodness of fit $= [\Sigma(|F_o| - |F_c|)^2/(N_{obsd} - N_v)]^{1/2}$

ence 13. The hydrogen atoms were placed in idealized positions and after anisotropic refinements for the nonhydrogen atoms and isotropic refinements for hydrogens the refinements converged at R_1=0.042, 0.046, 0.059, and 0.033, R_2=0.046, 0.044, 0.059 and 0.034, respectively for the four chelates; for definitions see Table 1. All calculations were carried out on a NOVA 3 minicomputer using the SHELXTL program package. The atomic coordinates for the nonhydrogen atoms and U_{eq} values are given in Table 2. Listings of anisotropic temperature factors, observed and calculated structure factors and hydrogen positional parameters are available from the authors (M.-L. R.).

Infrared spectroscopy. The spectra were recorded between 4000 and 200 cm^{-1} on a Perkin-Elmer 577 grating infrared spectrometer using KBr pellets.

Thermal analysis. The TG/DTG data were

Table 2. Atomic coordinates (x10^4) and U_{eq} values (x10^3, Å^2) (a) for $Pd(DPDTC)_2$, (b) for $Pd(DBDTC)_2$, (c) for $Pd(DIBDTC)_2$ and (d) for $Pd(FDEDTC)_2$. Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalised U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
$Pd(DPDTC)_2$, molecule *a*				
Pd	5000	0	5000	48(1)
S(1)	7886(3)	220(1)	5634(1)	58(1)
S(2)	5747(3)	−321(1)	6672(1)	56(1)
N	9046(7)	−85(3)	7595(4)	51(3)
C(1)	7754(10)	−66(3)	6770(5)	47(4)
C(2)	8913(10)	−363(4)	8543(5)	56(4)
C(3)	9760(13)	−1137(6)	8831(8)	87(5)
C(4)	8967(16)	−1699(5)	8093(9)	105(6)
C(5)	10722(11)	208(5)	7647(7)	66(4)
C(6)	11043(14)	973(7)	8141(11)	125(7)
C(7)	9788(21)	1489(7)	7962(13)	154(9)
$Pd(DPDTC)_2$, molecule *b*				
Pd)	5000	0	0	50(1)
S(1)	4947(3)	1075(1)	895(2)	59(1)
S(2)	5790(3)	941(1)	−883(2)	58(1)
N	5552(9)	2271(3)	−74(5)	56(3)
C(1)	5429(9)	1552(4)	−34(5)	52(5)
C(2)	5127(11)	2757(4)	653(7)	63(5)
C(3)	3280(11)	2979(5)	314(7)	77(6)
C(4)	2857(15)	3429(6)	1091(9)	89(6)
C(5)	5979(11)	2657(4)	−882(6)	61(5)
C(6)	7831(10)	2877(4)	−570(6)	62(5)
C(7)	8177(12)	3362(5)	−1338(7)	81(6)
$Pd(DBDTC)_2$				
Pd	0	5000	5000	69(1)
S(1)	1964(4)	9090(2)	1588(3)	85(1)
S(2)	−1382(4)	9205(2)	1078(3)	88(1)
N	632(10)	8143(5)	3038(7)	82(4)
C(1)	420(14)	8711(7)	2038(10)	80(6)
C(2)	2247(17)	7770(9)	3847(11)	102(7)
C(3)	2533(19)	6837(10)	3200(18)	125(9)
C(4)	4085(28)	6490(15)	3921(26)	163(13)
C(5)	4630(21)	5709(15)	3109(19)	184(14)
C(6)	−701(15)	7876(7)	3404(19)	94(6)
C(7)	−883(16)	8645(10)	4352(11)	106(7)
C(8)	−2397(19)	8479(10)	4567(13)	145(8)
C(9)	−2630(20)	9199(12)	5499(15)	153(9)

Table 2. Continued.

$Pd(DIBDTC)_2$				
Pd	2464(1)	1426(1)	2340(1)	53(1)
ligand *a*				
S(1)	4121(3)	3141(2)	8186(2)	68(1)
S(2)	3496(3)	2641(2)	6513(2)	68(1)
N	5400(7)	1892(6)	7397(4)	55(1)
C(1)	4494(8)	2472(7)	7366(6)	56(3)
C(2)	5644(10)	1342(8)	6676(6)	82(4)
C(3)	6192(14)	2017(13)	6082(9)	115(8)
C(4)	7247(16)	2437(15)	6436(10)	149(9)
C(5)	6340(14)	1362(13)	5342(7)	149(9)
C(6)	6142(9)	1708(9)	8165(7)	72(5)
C(7)	6006(11)	700(9)	8540(7)	87(5)
C(8)	4826(11)	422(11)	8624(9)	120(8)
C(9)	6759(12)	626(11)	9370(8)	122(8)
ligand *b*				
S(1)	1475(2)	4507(2)	8181(2)	64(1)
S(2)	790(2)	4034(2)	6516(2)	65(1)
N	−460(7)	5273(6)	7342(5)	57(1)
C(1)	467(7)	4669(7)	7348(6)	46(2)
C(2)	−1185(8)	5533(7)	6610(5)	53(3)
C(3)	−1087(10)	6598(8)	6300(6)	72(5)
C(4)	127(12)	6778(12)	6145(10)	174(10)
C(5)	−1901(11)	6810(10)	5561(7)	89(6)
C(6)	−694(9)	5734(8)	8112(6)	67(5)
C(7)	−1182(13)	5074(12)	8685(7)	109(8)
C(8)	−2207(15)	4524(13)	8336(8)	145(9)
C(9)	−1353(13)	5622(12)	9445(7)	135(9)
$Pd(FDEDTC)_2$				
Pd	0	0	0	37(1)
S(1)	2768(1)	192(1)	380(1)	47(1)
S(2)	528(1)	2238(1)	914(1)	48(1)
N	3697(3)	2786(3)	1393(2)	36(1)
F(1)	2366(3)	5217(3)	174(2)	76(1)
F(2)	2603(4)	6703(3)	1472(2)	92(1)
F(3)	4672(3)	5921(3)	935(2)	81(1)
F(4)	5468(4)	383(3)	2568(3)	99(1)
F(5)	6286(4)	2498(4)	3201(2)	102(1)
F(6)	7649(3)	1256(4)	2306(2)	100(1)
C(1)	2492(3)	1865(3)	955(2)	37(1)
C(2)	3351(4)	4213(4)	1852(3)	43(1)
C(3)	3240(4)	5512(4)	1101(3)	53(1)
C(4)	5362(4)	2400(4)	1396(3)	42(1)
C(5)	6178(4)	1632(5)	2379(3)	57(1)

obtained on a Mettler TA 3000 TG 50 thermobalance for samples of *ca.* 10 mg under a nitrogen atmosphere (150 ml/min) at a heating rate of 20 °C/min. DSC curves were recorded on a Mettler TA 3000 DSC 20 system under a dynamic nitrogen atmosphere (150 ml/min) with heating rates of 5 and 10 °C/min. Sample sizes were about 3 mg. High-purity indium (≥99.999 %) was used for calorimetric and temperature calibrations.

Gas chromatography. Carlo Erba Fractovap

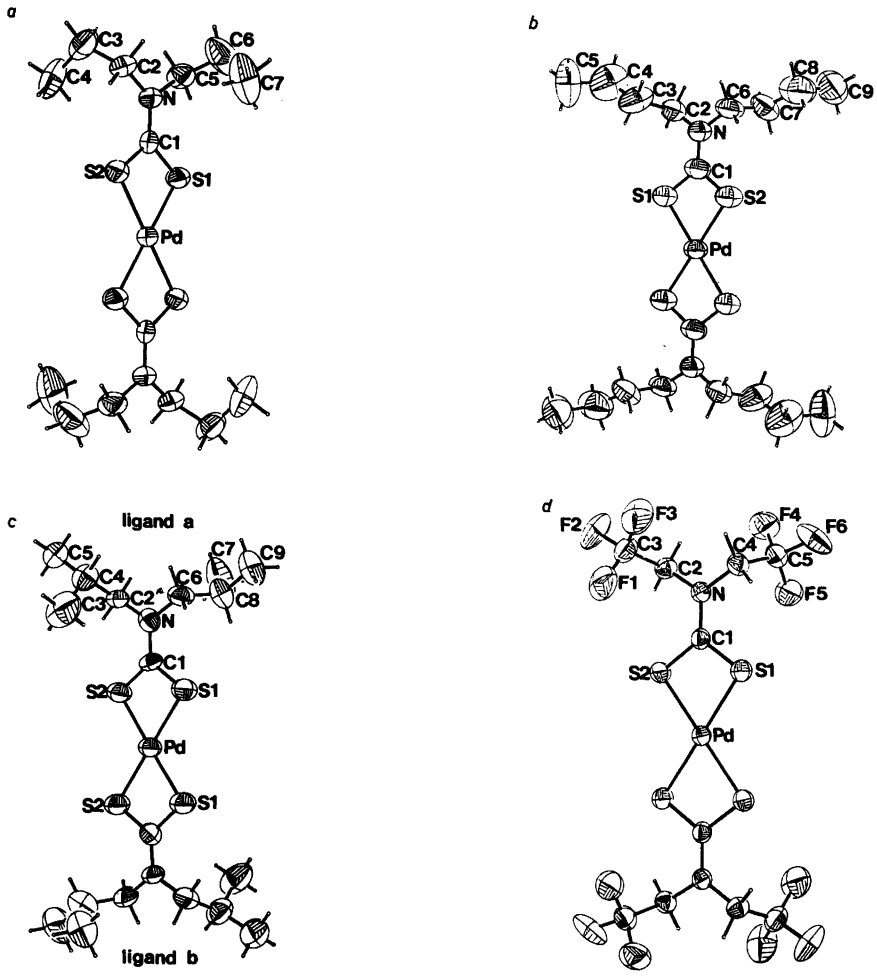


Fig. 1. Perspective drawings (a–d) showing the molecular structures and atomic numbering schemes for $Pd(DPDTC)_2$, $Pd(DBDTC)_2$, $Pd(DIBDTC)_2$, and $Pd(FDEDTC)_2$, respectively. In the case of $Pd(DIBDTC)_2$ the crystallographically independent ligands are distinguished by letters a and b. 50 % thermal ellipsoids are used with the exception of hydrogen atoms which are drawn artificially small.

Series 2150 and 2900 gas chromatographs were employed for splitless injections. On-column injections were performed with Carlo Erba Fractovap Series 4160 with LT programmer. The gas chromatographs were equipped with flame ionization detectors. Fused silica capillary columns with SP-2100 liquid phase (2 m×0.20 mm I.D., Hewlett-Packard) and OV-101 liquid phase (4 m×0.30 mm I.D., Orion Analytica) and glass capillary column coated with OV-101 liquid phase (4 m×0.30 mm I.D., prepared by Dr. S. Räisänen) were used for the results presented. Helium or nitrogen were used as the carrier gas.

RESULTS AND DISCUSSION

X-ray crystallography. The structures and the atomic numbering schemes are shown for the four chelates in Fig. 1. The bond lengths and angles are collected in Tables 3 and 4 along with the data for $Pd(DEDTC)_2$.[14] $Pd(DPDTC)_2$ has two crystallographically distinct molecules, which both have the palladium atom at a center of symmetry. The molecules are designated *a* and *b* in Tables 3 and 4, and have been given the same numbering scheme.

Table 3. Bond distances (Å) for $Pd(DEDTC)_2$, $Pd(DPDTC)_2$, $Pd(DBDTC)_2$, $Pd(DIBDTC)_2$, and for $Pd(FDEDTC)_2$.

Bond	$Pd(DEDTC)_2$[a]	$Pd(DPDTC)_2$ (molecule *a*)	$Pd(DPDTC)_2$ (molecule *b*)	$Pd(DBDTC)_2$	$Pd(DIBDTC)_2$ (ligand *a*)	$Pd(DIBDTC)_2$ (ligand *b*)	$Pd(FDEDTC)_2$
Pd–S(1)	2.317(3)	2.323(2)	2.323(2)	2.316(3)	2.316(3)	2.304(3)	2.320(1)
Pd–S(2)	2.315(3)	2.322(2)	2.329(2)	2.313(4)	2.321(3)	2.323(3)	2.316(1)
S(1)–C(1)	1.73(1)	1.733(8)	1.730(9)	1.727(14)	1.728(10)	1.705(9)	1.703(3)
S(2)–C(1)	1.70(1)	1.706(8)	1.730(8)	1.691(10)	1.719(9)	1.700(10)	1.699(3)
C(1)–N	1.32(1)	1.309(8)	1.306(9)	1.311(13)	1.317(13)	1.357(12)	1.349(4)
N–C(2)	1.49(2)	1.469(10)	1.473(12)	1.452(15)	1.462(13)	1.424(11)	1.457(4)
N–C(4)	1.48(2)	—	—	—	—	—	1.462(4)
N–C(5)	—	1.485(12)	1.486(12)	—	—	—	—
N–C(6)	—	—	—	1.459(17)	1.459(12)	1.481(13)	—

[a] Ref. 14.

Table 4. Bond angles (deg) for $Pd(DEDTC)_2$, $Pd(DPDTC)_2$, $Pd(DBDTC)_2$, $Pd(DIBDTC)_2$, and for $Pd(FDEDTC)_2$.

Angle	$Pd(DEDTC)_2$[a]	$Pd(DPDTC)_2$ (molecule *a*)	$Pd(DPDTC)_2$ (molecule *b*)	$Pd(DBDTC)_2$	$Pd(DIBDTC)_2$ (ligand *a*)	$Pd(DIBDTC)_2$ (ligand *b*)	$Pd(FDEDTC)_2$
S(1)–Pd–S(2)	75.5(1)	75.4(1)	75.5(1)	75.3(1)	75.4(1)	75.3(1)	75.1
Pd–S(1)–C(1)	86.1(4)	86.2(3)	86.8(3)	86.0(3)	86.8(3)	86.5(3)	86.2(1)
Pd–S(2)–C(1)	87.0(4)	86.9(3)	86.6(3)	87.0(5)	86.9(4)	86.0(3)	86.4(1)
S(1)–C(1)–S(2)	111.5(7)	111.4(4)	110.8(4)	111.7(6)	110.7(6)	112.1(5)	112.3(2)
S(1)–C(1)–N	123.1(9)	123.7(7)	124.4(7)	124.1(8)	124.5(7)	123.7(7)	123.8(2)
S(2)–C(1)–N	125.5(9)	124.8(7)	124.8(7)	124.2(10)	124.8(7)	124.1(7)	123.9(2)
C(1)–N–C(2)	120(1)	122.6(7)	121.1(8)	121.2(11)	121.3(8)	122.8(8)	120.1(3)
C(1)–N–C(4)	123(1)	—	—	—	—	—	121.1(3)
C(1)–N–C(5)	—	121.9(7)	122.3(7)	—	—	—	—
C(1)–N–C(6)	—	—	—	121.9(9)	121.7(8)	119.3(8)	—
C(2)–N–C(4)	117(1)	—	—	—	—	—	118.8(2)
C(2)–N–C(5)	—	115.4(5)	116.3(6)	—	—	—	—
C(2)–N–C(6)	—	—	—	116.9(9)	116.7(8)	117.8(8)	—

[a] Ref. 14.

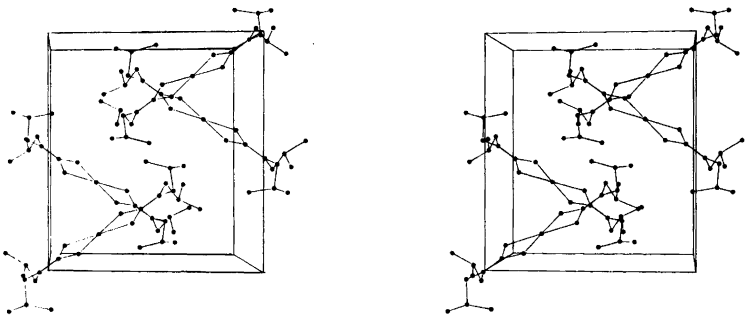


Fig. 2. A stereoview showing the packing of molecules in the unit cell of $Pd(DIBDTC)_2$.

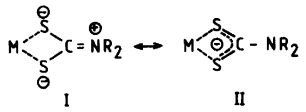
$Pd(DBDTC)_2$ and $Pd(FDEDTC)_2$ have the center of symmetry at the palladium atom while $Pd(DIBDTC)_2$ does not have internal crystallographic symmetry. The di-isobutyldithiocarbamate ligands are chemically equivalent, however, which is indicated by the numbering scheme in Fig. lc.

Intramolecular interactions between hydrogen in the α-carbon of the ligand substituents and sulfur are short (2.547–2.722 Å) in all the present palladium chelates. The corresponding short S···H-contacts have occurred in the structures of nickel(II) di-isopropyl- and di-isobutyldithiocarbamate chelates.[15,16] Judging from intermolecular distances there is no clear evidence for hydrogen bonding in any of the four chelates, the molecules being held together by van der Waals forces. Fig. 2 shows the contents of unit cell and molecular packing for a representative chelate $Pd(DIBDTC)_2$.

When comparing the structural data with those available in the literature[17] it is noted that the ligand structure is only slightly changed upon coordination. The carbon–nitrogen bond C(1)-N has double bond character, typical of metal dialkyldithiocarbamate chelates. Furthermore, the bonds and angles involving the chelating sulfur atoms are not significantly different in any of the chelates and their values are in agreement with the data reported recently by Nikolov.[18]

Infrared spectroscopy. Infrared spectra of metal chelates of dialkyl-substituted dithiocarbamic acids tend to be complicated by the strong coupling of peaks. Three pure uncoupled stretching frequencies, strong and broad $\nu(C{\cdots}N)$, medium strong $\nu(C{\cdots}S)$, and in the far infrared also medium strong $\nu(M-S)$, are characteristic for the spectra. Since they characterize the ligand substitution as well as the central atom the identification of chelates is relatively easy (see Table 5).

Metal dialkyldithiocarbamate chelates have the two resonance forms I and II. Form I reflects



I II

the electron releasing tendency of the R_2N-group. The tendency of the amine group to donate electrons to the sulfur atoms increases their electron donating capacity and their ability

Table 5. Infrared spectral characteristics of some palladium dithiocarbamate chelates.

Metal chelate	$\nu(C{\cdots}N)$ (cm^{-1})	$\nu(C{\cdots}S)$ (cm^{-1})	$\nu(M{-}S)$ (cm^{-1})
$Pd(DEDTC)_2$	1521	990	360
$Pd(DPDTC)_2$	1514	972	355
$Pd(DBDTC)_2$	1510	975	358
$Pd(DIBDTC)_2$	1506	980	362
$Pd(FDEDTC)_2$	1464	990	384

Table 6. TG/DTG data for the palladium chelates.

Metal chelate	Weight loss (%)	Temperature range (°C)	DTG peak temp. (°C)
$Pd(DEDTC)_2$[a]	92	235–440	410
$Pd(DPDTC)_2$[a]	93	240–445	418
$Pd(DBDTC)_2$[a]	93	235–445	420
$Pd(DIBDTC)_2$	96	240–445	418
$Pd(FDEDTC)_2$	100	140–360	270

[a] For these chelates TG data measured with a different apparatus have been reported in Refs. 1 and 12. The present values differ slightly from those reported.

Table 7. DSC data for the palladium chelates with esd's in the parentheses.

Metal chelate	M.p. (°C)	Other peaks (°C)[a]	Heat of fusion (kJ/mol)
$Pd(DEDTC)_2$	243	335,[b] 384[c]	39.03(47)
$Pd(DPDTC)_2$	149	343, 371	30.24(56)
$Pd(DBDTC)_2$	109	345, 362	29.41(31)
$Pd(DIBDTC)_2$	189	330, 388	30.48(25)
$Pd(FDEDTC)_2$	161	240, 303	39.57(44)

[a] All endothermic peaks. [b] Onset temperature. [c] Peak temperature.

to form strong chelates with transition metal ions. Thus the C–N bond has a significant double bond character.

IR data in Table 5 indicate that the significance of resonance form I decreases with the increasing length of the alkyl group as proposed by Kellner.[19] This effect is inferred from the decrease of the stretching frequency $\nu(C\cdots N)$. The effect is very small, the accuracy of the C–N bond lengths, determined by X-ray diffraction, is not sufficient to show the same trend.

The fluorinated chelate has a much lower $C\cdots N$ stretching frequency and somewhat longer C–N bond than in the nonfluorinated chelates. The S–C bond lengths are also slightly shorter, and the $\nu(S\cdots C)$ somewhat higher in the fluorinated compound. These facts indicate that the resonance structure II is favored in $Pd(FDEDTC)_2$.

Thermal analysis. The TG/DTG and DSC data are presented in Tables 6 and 7 which contain for comparison also the values for the diethyldithiocarbamate chelate $Pd(DEDTC)_2$. All chelates first undergo fusion at temperatures ranging from 109 to 243 °C followed by nearly complete volatilization. The fluorinated chelate has clearly

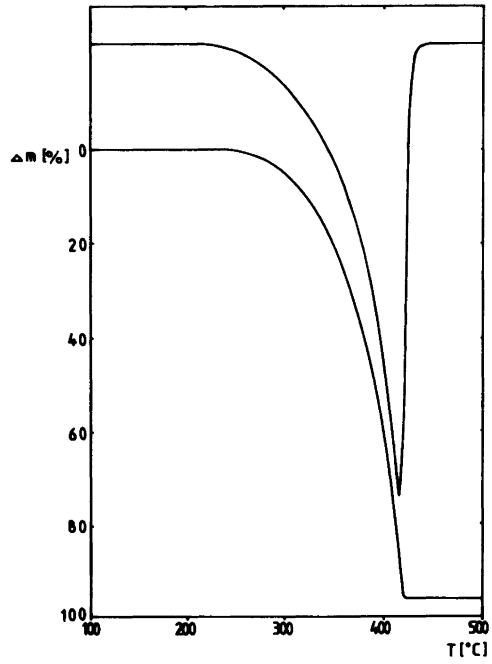


Fig. 3. TG and DTG curves of $Pd(DIBDTC)_2$ in nitrogen atmosphere. Heating rate 20 °C/min.

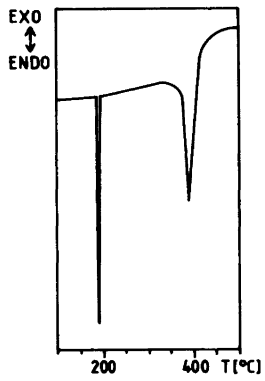


Fig. 4. DSC curve of $Pd(DIBDTC)_2$ in nitrogen atmosphere. Heating rate 5 °C/min.

the highest volatility in spite of its high molecular weight. It also shows no decomposition while for the other compounds the TG data indicate slight degradation of the order of a few percent.

Except for the behavior of the $Pd(FDEDTC)_2$, it is difficult to recognize any other clear trends between the structure and the volatility or the fusion data. The dibutyldithiocarbamate chelate has the lowest melting point and heat of fusion while the diethyl-substituted chelate has by far the highest melting point. On the other hand, there are no significant differences between the volatility of these chelates. It should be noted, however, that the volatilization takes place after complete fusion and experiments performed in vacuum might give different results.

Gas chromatography. The palladium chelates are sufficiently volatile and thermally stable for gas chromatography on short nonpolar capillary columns by using splitless or on-column injections. The influence of fluorination of palladium diethyldithiocarbamate on the volatility is clearly seen in the gas chromatographic characteristics: the fluorinated palladium chelate elutes first and at much lower temperatures than other non-fluorinated ones. Thus fluorine substitution in the ligand results in a marked increase in volatility. The lower column temperatures needed for elution decrease also the possibility of thermal decomposition.

There are problems with splitless injection in the simultaneous separation of the fluorinated and the other palladium chelates studied; the great temperature differences of vaporization cause severe tailing for the nonfluorinated che-

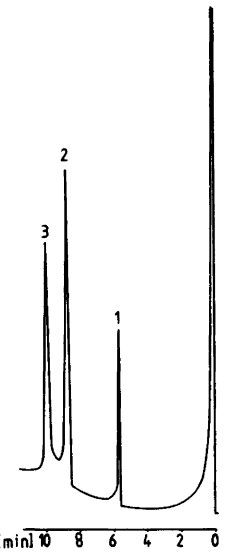


Fig. 5. Gas chromatographic elution of (1) $Pd(FDEDTC)_2$, (2) $Pd(DEDTC)_2$, and (3) $Pd(DIBDTC)_2$ on fused silica OV−101 by using on-column injection. Conditions: det. 300 °C; oven 70 °C (3 min)−150 °C (0 min)−255 °C (1 min)−300 °C (0 min), heating rates 15 °C/min, 25 °C/min, and 25 °C/min, resp; N_2: 7 ml/min and make-up gas 5 ml/min.

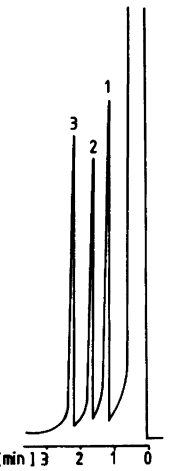


Fig. 6. Separation of (1) $Pd(DEDTC)_2$, (2) $Pd(DPDTC)_2$, and (3) $Pd(DBDTC)_2$ on glass capillary column OV-101 by using splitless injection. Conditions: inj./det. 275 °C; oven 170 °C (0 min) – 270 °C (0 min), heating rate 39 °C/min; He: 8 ml/min.

lates as an indication of adsorption in an injection cavity. With on-column injection the separation succeeds very well (*e.g.* Fig. 5). Splitless injection applied to the separation of the nonfluorinated chelates is successful except for the dipropyl- and di-isobutyldithiocarbamates with the same retention time (Fig. 6). The similar volatility of the dipropyl- and di-isobutyldithiocarbamate chelates has also been observed in the vapor pressure measurements of nickel and copper chelates.[20] Hartmetz *et al.*[21] have compared splitless and on-column injection techniques with fluorinated diethyldithiocarbamates and they have found on-column injection to widen the linearity of calibration curves for some labile metal chelates when using glass capillary columns. For stable metal chelates and with fused silica columns they found only small or no differences.

Volatility trends and molecular properties. Correlation of volatility and molecular structure of metal complexes has been a subject of some studies.[4–6] In the present work a more detailed analysis would be possible in principle. Volatility is a function of intermolecular interactions, in gas chromatographic circumstances vaporization takes place from liquid or solvated state. None of the present structural methods probe directly the complexes in this state. On the other hand it can be assumed that the major interactions operative in liquid state must somehow also show up in the solid state.

For the palladium dialkyldithiocarbamate chelates studied in this work, a correlation between the fluorinated and nonfluorinated compounds and the volatility can be found. The fluorinated chelate is much more volatile than the nonfluorinated derivatives. The principal reason is the fluorination itself, the molecule is surrounded by fluorine atoms, which decrease intermolecular interactions in the same way as in the fluorinated aliphatic hydrocarbons. The secondary effect may be a decrease in the polarization of the S_2CN system due to the electronic effect of the fluorine atoms.

The nonfluorinated chelates have a distinct volatility order. The small variations in the structures of the central $Pd(S_2CN)_2$ fragments do not have any clear trends which could be correlated with volatility. The principal effects are the molecular weight and shape. Increasing molecular weight enhances the polarizability of the molecule and makes it less volatile. These effects taken together qualitatively explain the volatility order: DEDTC<DPDTC≃DIBDTC<DBDTC. The closest intermolecular contacts in solid state are mainly between the ligand terminal groups and the palladium atoms. These interactions are very similar in the nonfluorinated derivatives and cannot be used for the interpretation of the volatility order.

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