Inorganica Chimica Acta, *132* (1987) 99–103

The Effect of Fluorination on the Thermal Properties and Crystal Structure of Bis[*N*,*N*-di(trifluoroethyl)dithiocarbamato]nickel(II)

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(Received January 15, 1987)

Abstract

The structure of bis[*N*,*N*-di(trifluoroethyl)dithiocarbamato]nickel(II) has been determined by single-crystal X-ray diffraction methods. The compound forms strongly pleochroic monoclinic crystals in the space group $P2_1/n$ (no. 14, C^5_{2h}) with $a = 8.519(2)$, $b = 8.912(1)$, $c = 11.098(2)$ Å, $\beta = 103.18(2)°$ and $Z = 2$. The final R value for 1002 reflections was 0.040. The nickel atom is chelated in a planar array by two symmetric bidentate *N*,*N*-di(trifluoroethyl)dithiocarbamate ligands, ⟨Ni–S⟩ 2.19_9 Å. The known volatility of the compound is explained by the fact that there are no strong intermolecular interactions. The temperature factor coefficients of the compound and its non-fluorinated analogue correlate with the known fragmentation patterns in the gas phase. The resonance form including a double bond C=N is characterized both by IR and NMR spectra and the geometry around the nitrogen atom of the *N*,*N*-di(trifluoroethyl)dithiocarbamate ligand. The electronic properties of the chelate are dominated by the fluorine atoms, and to a minor extent by the electron-withdrawing capacity of the central atom.

Introduction

Dialkyldithiocarbamates have a wide range of applications as, for example, herbicides, fungicides and vulcanization accelerators [1]. The extractability of their metal complexes as well as their volatility and thermal stability has permitted them to be used in gas-chromatographic determinations [2, 3]. The selective and sensitive gas chromatographic method using dialkyldithiocarbamate ion as a ligand has been applied to quantitative trace analyses of some metals in real samples, too [4–8]. Fluorination of the diethyldithiocarbamate ion (dedtc hereafter) leads to a large increase in volatility without change in thermal stability, and to rise in vapour pressure of the order of more than two decades [9]. On the other hand, fluorination has been reported to decrease the gas phase stability [10]. In a recent review of the thermal behaviour of metal dithiocarbamates it was stated that although there are much data, one cannot establish any general correlation between the volatility and the structure [11]. In this work we have elucidated the correlations between the structure of bis[*N*,*N*-di(trifluoroethyl)dithiocarbamato]nickel(II), Ni(fdedtc)$_2$ hereafter, and both the thermal behaviour and volatility by determining its crystal structure and studying its properties with NMR and IR spectroscopy. The characteristics of this compound will be compared with the non-fluorinated analogue [12], and in some instances with the corresponding palladium complexes [13, 14].

Experimental

Syntheses

Sodium *N*,*N*-di(trifluoroethyl)dithiocarbamate dihydrate was synthesized from bis(trifluoroethyl)-amine (PCR International, Gainsville, U.S.A.) using a technique similar to that described in ref. 15. *Anal.* Found: C, 19.4; H, 2.5; F, 36.2; N, 4.5; S, 20.4. Calc. for $C_5H_4F_6NS_2 \cdot 2H_2O$: C, 19.05; H, 2.6; F, 36.2; N, 4.4; S, 20.35%. Water was analyzed thermogravimetrically: found 11.5%, calc. 11.4%.

Ni(II)(fdedtc)$_2$ was then prepared as described in ref. 15; δ_H (60 MHz; solvent $CDCl_3$; standard Me_4Si) 4.23 [2H, q, *J*(FH) 7.9 Hz].

Ni(dedtc)$_2$ was prepared as before [2]; δ_H (60 MHz; solvent $CDCl_3$; standard Me_4Si) 3.48 [2H, q, *J* 7.0 Hz, CH_3CH_2] 1.18 [3H, t, *J* 7.0 Hz, CH_3CH_2].

X-ray Study

The strongly pleochroic (green and red) crystals used in X-ray diffraction study were recrystallized from a methanol solution. Data were collected at ambient temperature on a Syntex P2$_1$ diffractometer. Lattice parameters were obtained from least-squares refinement of 21 high-angle, well-centered reflections (see Table I). During the intensity collection, three check reflections were measured after every 39 reflections. The intensities of these showed only

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TABLE I. Crystal and Intensity Collection Data

Molecular formula	$C_{10}H_8F_{12}N_2NiS_4$
Molecular weight	454.03
$F(000)$	563
a (Å)	8.519(2)
b (Å)	8.912(1)
c (Å)	13.098(2)
β (°)	103.18(2)
V (Å^3)	968.2(3)
Z	2
D_c (g cm^{-3})	1.96
D_m	1.95
Space group	$P2_1/n$ (no. 14, C_{2h}^5)
Crystal dimensions (mm)	0.14 × 0.12 × 0.19
Radiation	Mo Kα (λ = 0.71069 Å)
2θ limits	$5° < 2\theta < 52°$
Scan rate	2.0° to 29.3°/min
Absorption coefficient (cm^{-1})	15.3
No. independent reflections measured	2165
Unique data used	1002
R	0.040
R_w	0.032

TABLE II. Fractional Coordinates for Ni(fdedtc)$_2$

Atom	x/a	y/b	z/c
Ni	0.0000	0.0000	0.0000
S(1)	0.2649(2)	−0.0107(2)	0.0351(1)
S(2)	0.0438(2)	−0.2098(2)	0.0901(1)
N	0.3619(5)	−0.2689(5)	0.1378(3)
C(1)	0.2414(6)	−0.1763(6)	0.0941(4)
C(2)	0.3299(8)	−0.4107(7)	0.1846(5)
C(3)	0.3155(9)	−0.5398(7)	0.1086(6)
C(4)	0.5294(7)	−0.2316(8)	0.1379(5)
C(5)	0.6163(8)	−0.1576(8)	0.2379(6)
F(1)	0.2251(5)	−0.5098(5)	0.0151(3)
F(2)	0.2537(5)	−0.6594(4)	0.1456(3)
F(3)	0.4575(5)	−0.5800(4)	0.0925(3)
F(4)	0.5479(5)	−0.0316(5)	0.2570(3)
F(5)	0.6267(5)	−0.2426(5)	0.3207(3)
F(6)	0.7641(5)	−0.1221(5)	0.2323(3)
H(21)	0.417(6)	−0.437(5)	0.249(4)
H(22)	0.234(6)	−0.397(5)	0.212(3)
H(41)	0.596(5)	−0.325(5)	0.131(3)
H(42)	0.533(4)	−166(4)	0.079(3)

statistical variation. The intensities were corrected for background, polarization, and Lorentz factors. Empirical absorption corrections were made based on ψ-scan data. The details of the data collection and processing are given in Table I. The structure was solved by the heavy atom method of the XTAL system using atomic scattering factors included in the program [16]. Dispersion corrections were applied for Ni, S, F, and C [17]. The final full-matrix least-squares refinement applied to anisotropic non-hydrogen atoms and isotropic hydrogen atoms yielded an R value of 0.040 ($R_w = 0.032$, $1/\sigma^2(F_o)$ weights). Agreement indices were defined as follows: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. The final fractional atomic coordinates are shown in Table II. The data reported in Table III were obtained by the VAXRAY system [18].

All the calculations were performed on a VAX 8600 computer.

Spectroscopy

The IR spectra were run from KBr discs on a Perkin-Elmer grating infrared spectrophotometer 577. A polystyrene film was used in calibration. The ^{1}H-NMR spectra were run on a Jeol JNM-PMX 60 spectrometer.

Results and Discussion

The bond lengths and angles for the title compound and its non-fluorinated analogue are shown in Fig. 1 with the numbering scheme. As can be seen from the bonding parameters, fluorination does not produce major differences in the molecular structure.

The coordination around the Ni(II) ion is planar. According to earlier studies, the only cations forming planar diethyldithiocarbamato complexes are those of Ni(II), Pd(II) and Pt(II), each representing the d^8 electronic configuration [12, 13, 19]. However, the difference in effective ionic radii of the central

TABLE III. Information on Planes Containing the Atoms N, C(1), C(2) and C(4) in Ni(fdedtc)$_2$, Ni(dedtc)$_2$, Pd(fdedtc)$_2$ and Pd(dedtc)$_2$

	Ni(fdedtc)$_2$	Ni(dedtc)$_2$^{a}	Pd(fdedtc)$_2$^{a}	Pd(dedtc)$_2$^{a}
χ^2	1.48	5.83	6.96	0.07
ϵ^b (°)	4.2(2)	5.7(3)	2.73(11)	2.9(5)
d^c, N	0.005	0.019	0.007	0.003
d, C(1)	−0.003	−0.006	−0.002	−0.001
d, C(2)	−0.004	−0.011	−0.005	−0.001
d, C(4)	−0.004	−0.013	−0.005	−0.002

[a] The values are calculated from the data reported in refs. 12, 14, and 13, respectively. [b] Angle between the planes MS$_2$ and NC(1)C(2)C(4). [c] Deviation from the least-squares plane (Å).

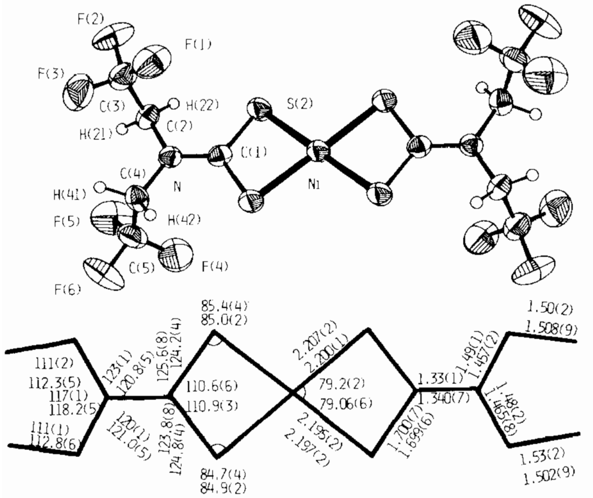


Fig. 1. The molecular structure, atom numbering, and bond lengths and angles for Ni(fdedtc)$_2$. The ORTEP drawing shows the thermal ellipsoids at the 50% probability level. The upper values of the bonding parameters refer to Ni(dedtc)$_2$ and the lower values to Ni(fdedtc)$_2$. The C–F bond lengths range from 1.309 up to 1.328 (e.s.d.s 0.008) Å, and the F–C–F angles from 105.6 up to 113.6° with e.s.d.s of 0.6°.

atoms results in differences in metal–sulfur bonds. The effective ionic radii of Ni(II), Pd(II), and Pt(II) are 0.63, 0.78, and 0.74 Å, respectively [20]. In Pd(dedtc)$_2$ and Ni(dedtc)$_2$ (and in their fluorinated analogues) the Pd–S and Ni–S bond lengths are approximately 2.3 and 2.2 Å, respectively, while in Pt(dedtc)$_2$ it is 2.3 Å. Another difference is seen in the angle between the metal–sulfur and C(1)NC(2)C(4) planes (Table III); the angle is smaller for the Pd chelates.

Tavlaridis and Neeb have shown that the fluorination of the alkyl group decreases ΔH_S by 12.2%, while ΔS_S (subscript S = sublimation) is increased by 8.3% [15]. The former value suggests that fluorination decreases intermolecular interactions in the solid state, whereas the latter implies increase of the number of microstates in the gas phase. There are two short intramolecular S–H distances, about 2.6 Å. The angles C(2)–H(22)–S2 and C(4)–H(42)–S(1) are rather small, 81(2)° and 108(3)°, respectively. Moreover, the non-bonding electron pairs of the sulfur atoms do not point towards the hydrogens. Thus, the existence of intramolecular hydrogen bonds is uncertain. It must be emphasized, that there are no intermolecular S–H distances shorter than 3.05 Å (the sum of the corresponding van der Waals radii), which are usually thought to be the major factor dominating the packing of the metal dithiocarbamates [21]. There are only a few other possible intermolecular interactions in Ni(fdedtc)$_2$. The hydrogen atom H(22) has two distances to the fluorine atoms, which are shorter than the sum of the corresponding van der Waals radii: H(22)–F(4)^i (where i refers to a symmetry operator $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) and H(22)–F(2)^i, 2.79(5) and 2.81(4) Å, respectively. These distances are so long, however, that the hydrogen bonding is likely to have a minor role. In addition, there is a rather long fluorine–fluorine distance, namely F(3)–F(6)^i, 2.924(5) Å. It may be worth adding that the Ni–H(2)^i is 3.25(5) Å, which is a considerably longer value than the corresponding value of 2.68 Å in bis(*N*,*N*-diisobutyldithiocarbamato)nickel(II) [21].

A mass spectrometric study carried out on several metal dialkyldithiocarbamate chelates revealed that fluorination of the alkyl group decreases the gas phase stability [10]. This was illustrated very clearly in the difference between the relative intensities of the $(ML_2)^+$ ions of the fluorinated and non-fluorinated nickel and palladium chelates (Ni: 28 and 100; Pd: 28 and 93, respectively). The most intensive ion in the mass spectrum of the fluorinated chelate was $(R_2NCS)^+$. Another difference in the spectra was the non-existence of the $(R_2N)^+$ ion for these chelates.

It has been suggested that anisotropic temperature factor coefficients or their equivalent values, U_{eq}, could be used as indicators of the thermal decomposition processes [22]. The equivalent values U_{eq} of the anisotropic temperature factors for the non-hydrogen atoms of both Ni(II) and Pd(II) chelates are shown in Table IV. When we compare the ΔU_{eq} values, it is

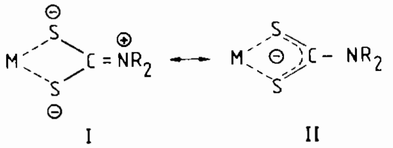
TABLE IV. Thermal Parameters U_{eq}^{a} for the Compounds Ni(fdedtc)$_2$, Ni(dedtc)$_2$, Pd(fdedtc)$_2$ and Pd(dedtc)$_2$

Atom	Ni(fdedtc)$_2$		Ni(dedtc)$_2$		Pd(fdedtc)$_2$		Pd(dedtc)$_2$	
	U_{eq}	ΔU_{eq}^{b}	U_{eq}	ΔU_{eq}	U_{eq}	ΔU_{eq}	U_{eq}	ΔU_{eq}
Ni	0.0410	0.0038	0.0423	0.0000	0.037	0.001	0.0391	0.0000
S(1)	0.0498	0.0126	0.0499	0.0076	0.047	0.011	0.0489	0.0098
S(2)	0.0515	0.0143	0.0519	0.0098	0.048	0.012	0.0563	0.0172
N	0.0372	0.0000	0.0540	0.0117	0.036	0.000	0.0524	0.0133
C(1)	0.0381	0.0009	0.0451	0.0028	0.037	0.001	0.0453	0.0062
C(2)	0.0429	0.0057	0.0654	0.0231	0.043	0.007	0.0682	0.0291
C(4)	0.0456	0.0084	0.0707	0.0284	0.042	0.006	0.0695	0.0304

^{a}Defined as one third of the trace of the U_{ij} tensor. ^{b}The ΔU_{eq} values for the compounds are obtained by taking the smallest value and substracting it from the others.

readily seen that the values for the alkyl carbons are clearly smaller than those for the fluorinated species. Another more interesting feature in the light of the thermal stability is the differences in the $NiS_2C(1)N$ moieties. The base atom, with which we compare the others, is N for the fluorinated chelates, because it has the smallest U_{eq} value. Since the C(1) atoms also have small values, the $(R_2N)^+$ ions are not visible in the mass spectrum. The base atom for the non-fluorinated chelates is the central metal atom, which seems to correlate with the high intensities of the molecular ions. The relative difference in ΔU_{eq} values of the S atoms in $Pd(dedtc)_2$ might be reflected in the smaller intensity of the $(PdL_2)^+$ ion.

The dithiocarbamate system can be represented by the following resonance structures (Scheme 1). If



Scheme 1.

the resonance form **I** is dominant, then there is a double bond between nitrogen and carbon C(1). Moreover, nitrogen should lie in a plane formed by N, C(1), C(2) and C(4). As we can see from Fig. 1, the C(1)–N bond in $Ni(fdedtc)_2$ and $Ni(dedtc)_2$ do not differ significantly and their values indicate a clear double bond character. If we make use of the equation of Bonamico *et al.* [12], the double bond order can be said to decrease from 65% to 60% upon fluorination. However, the ν(C–N) wavenumbers for $Ni(dedtc)_2$ and $Ni(fdedtc)_2$ do differ: 1522 and 1467 cm^{-1}, respectively. The lower value of the fluorinated complex may be mainly due to the increased mass of the alkyl groups, and not merely because of enhanced single-bond character of the C(1)–N bond. On the other hand, the fluorination has probably improved the planarity around nitrogen in the Ni(II) complex (Table III). The χ^2 value of 5.83 for $Ni(dedtc)_2$ implies that the atoms N, C(1), C(2) and C(4) deviate from the least-squares plane at a 0.05 level of significance but not at the 0.01 level, *i.e.* the non-planarity is probably significant. In $Ni(fdedtc)_2$ the non-planarity is not significant. Surprisingly, the trend is opposite in the palladium chelates; in $Pd(dedtc)_2$ the non-planarity is highly significant, whereas in $Pd(fdedtc)_2$ it is not significant. However, in each compound there is a tendency for the nitrogen to lie on the opposite side of the least-squares plane to the carbon atoms.

The contribution from intermolecular interactions is minor; there are only two rather long F–H and one F–F distances, as stated already. Therefore, we may suppose that the geometric parameters in the $NiS_2C(1)NC(2)C(4)$ moieties are dominated by the electronic properties.

It seems that thermal equilibrium is also of importance and should be taken into consideration. The IR study of $Ni(dedtc)_2$ by Maltese *et al.* seems to corroborate this concept; a polycrystalline sample in 78 K shows an additional shoulder at 1504 cm^{-1} but in a N_2 matrix (10 K) only one absorption maximum at 1504 cm^{-1} [23]. This may indicate a phase transition. Attempts to trap $Ni(fdedtc)_2$ in a cryogenic Ar matrix are currently in progress.

In order to study further the resonance forms, ^1H NMR spectra were run for the Ni(II) compounds. Nikolov has shown that the variation in the nitrogen atom charge density is regulated by the central atom electron-withdrawing capacity in bis-diethyledithiocarbamate metal complexes [24]. He has reported the following correlation between the chemical shift $\delta(CH_2)$ and the stretching vibration wavenumber ν(C–N)

$$\delta(CH_2) = 0.00332\nu(C\text{–}N) - 1.16$$

This relation holds for $Ni(dedtc)_2$, but not for $Ni(fdedtc)_2$. If we use the observed value ν(C–N) of 1467 cm^{-1}, we obtain the calculated value $\delta(CH_2)$ of 3.71 ppm instead of the observed value of 4.23 ppm. Obviously, there must be a factor other than the central atom electron-withdrawing capacity involved. The chemical shifts imply the inductive effect due to the fluorine atoms.

Supplementary Material

A list of the structure factors and anisotropic thermal parameters are obtainable from the authors.

Acknowledgement

The authors wish to thank Mr. Mikko Väisänen for the discussions concerning the statistics.

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