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Crystal and Molecular Structure of Chlorotris[bis(2-hydroxyethyl)dithiocarbamato]tellurium(IV) Dihydrate

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The synthesis, properties, and crystal structure of the unusual mixed-ligand complex $TeCl[(HOC_2H_4)_2NCSS]_3 \cdot 2H_2O$ are described. The complex is monomeric in the crystalline state. The molecular structure shows a highly distorted pentagonal-bipyramidal coordination around tellurium featuring both strong and weak Te–S bonds in the equatorial plane and a strong Te–S bond and a rather weak Te–Cl bond in the axial positions. The complex is less stable than tetrakis(diethyldithiocarbamato)tellurium(IV). The chlorine atom and all the oxygen atoms participate in hydrogen bonding, and the packing arrangement in the unit cell seems to be mainly dictated by the hydrogen-bonding network.

Introduction

The dithiocarbamate group, $R_1R_2NCSS^-$, is a soft base and an important chelating disulfur ligand in post-transition-metal chemistry.[1] Foss, Husebye, and others,[2] from their extensive studies on sulfur ligand complexes of Te(IV), Te(II), and Se(II), have shown that, in all their complexes, the dithiocarbamate group (DTC) acts as a bidentate chelating ligand, though there is an unequal bonding participation of the two sulfur atoms from the same group. Also, the extent of chelation or the binding of the sulfur atoms to the metal depends on the substituents R_1 and R_2. Diethyldithiocarbamate (DEDTC) is one of the most effective chelating ligands due to electron-donating $R_1 = R_2 =$ ethyl groups and hence could form strong complexes of the type $Te^{IV}(DEDTC)_4$, but not mixed-ligand complexes. However, if electron-withdrawing groups such as C_2H_4OH are present, the complexing tendency of the ligand becomes weaker and allows other ligands such as halogens to enter the coordination sphere. This is evidenced by the fact that very few Te(IV) mixed-ligand complexes featuring DEDTC and halogens are encountered, whereas mixed-ligand complexes with DTC groups containing electron-withdrawing groups are known. There have been, to date, only two structure reports on mixed-ligand complexes of Te(IV), namely $PhTe(DEDTC)_3$[3] and $Te(DEDTC)_3Cl$. For $Te(DEDTC)_3Cl$, coordination around Te has been published,[4] but not its complete three-dimensional structure. Earlier, Aravamudan et al.[5] have reported $Te^{IV}(DEADTC)_2I_2$ (DEADTC = bis(2-hydroxyethyl)dithiocarbamate), but not its chloro, bromo, and thiocyanato analogues. These complexes with $Te(DEADTC)_3X$ (X = Cl, Br, or NCS^-) have also been successfully prepared now and characterized.[6] It is significant to point out that the chloride, bromide, and thiocyanate ions could displace only one of the DTC ligands from the $Te(DEADTC)_4$ complex, whereas iodide could displace two of the DTC ligands, being a better donor compared to the rest. Our detailed study of the structure of the complex $Te(DEADTC)_3Cl$ (denoted as TeL_3Cl) is reported here.

Experimental Section

A 2-mmol sample (0.32 g) of TeO_2 dissolved in 20 mL of 0.5 N NaOH was acidified with 2 N sulfuric acid. To this was added 40 mL of 20% aqueous methanol containing 20 mL of diethyldithiocarbamic acid, producing a deep red solution to which was added 4.7 g (64 mmol) of KCl dissolved in 20 mL of water. Pale red crystals appeared after 12 h. The presence of two water molecules in the crystal was detected during structure determination and later confirmed from infrared spectral results.

The crystal was found to be monoclinic, with space group $P2_1/n$ from preliminary photographs. The intensities of 3839 independent reflections from a crystal with dimensions 0.05 × 0.25 × 0.28 mm were collected on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). 2470 reflections with $I > 3\sigma(I)$ were considered observed and were used in structure analysis and refinement. The crystal data and the experimental conditions used during data collection are given in Table I.

Table I. Crystal Data and Data Collection Parameters

mol formula	$C_{15}H_{30}N_3O_6S_6TeCl \cdot 2H_2O$
mol wt	739.86
a, Å	10.310 (3)
b, Å	21.239 (4)
c, Å	13.331 (5)
β, deg	103.34 (3)
V, Å^3	2840.38
cryst system	monoclinic
systematic absences	$h0l$: $h + l = 2n + 1$ absent
	$0k0$: $k = 2n + 1$ absent
space group	$P2_1/n$
Z	4
d(calcd), g cm^{-3}	1.730
F(000)	1480
abs coeff (μ), mm^{-1}	1.49
θ interval, deg	2–25
$\omega/2\theta$ scan width ($\Delta\omega$), deg	$1.5 + 1.0 \tan\theta$
$\omega/2\theta$ aperture width, mm	$0.75 + 0.45 \tan\theta$
scan rate, deg min^{-1}	6.67–1.43
max recording time, s	50
check reflcns	two: (204), (303)
no. of reflcns collcd	3840 ($\pm h,k,+l$)
no. of reflcns $I > 3\sigma(I)$	2478

Structure Solution and Refinement

The conventional heavy-atom method was used in solving the structure. Full-matrix refinement with the SHELX-76[7] program of all non-hydrogen atoms with anisotropic thermal parameters reduced the *R* value to 0.035. A difference Fourier map constructed at this stage gave the locations of all the hydrogen atoms in the molecule. Methylene hydrogens had heights between 0.45 and 0.7 e/Å^3, and the hydrogens attached to the oxygen atoms showed peak heights ranging from 0.35 to 0.45 e/Å^3. In final refinement, hydrogen atoms were included with isotropic thermal parameters. The minimization function was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weighting function $w = 1.0/(\sigma^2(F_o) + 0.059|F_o|^2)$. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann[8] and for

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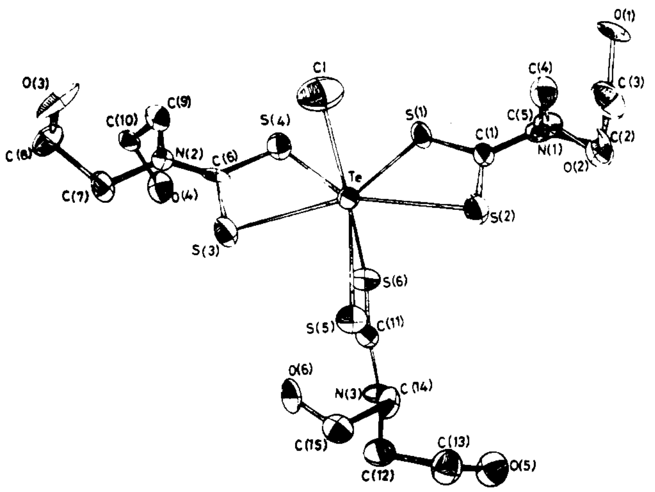

Figure 1. ORTEP drawing of TeL_3Cl.

hydrogen atoms from Stewart et al.[9] The anomalous dispersion correction factors for non-hydrogen atoms were taken from Cromer and Liberman.[10] Fractional coordinates and intramolecular bond distances and bond angles are given in Tables II and III, respectively. Anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameters for hydrogen atoms, and final structure factor amplitudes, both observed and calculated, are available as supplementary material.

Results and Discussion

The complex TeL_3Cl is stable indefinitely under dry conditions. It is soluble in most oxygen-containing polar organic solvents. However, unlike tetrakis(diethyldithiocarbamato)tellurium(IV), it is insoluble in benzene. As expected, the complex absorbs intensely in the ultraviolet region due to intraligand and charge-transfer (mainly S–Te) transitions. Addition of sodium diethyldithiocarbamate dissolved in methanol to the methanolic solution of the complex immediately brings about total displacement of the ligands and results in quantitative formation of tetrakis(diethyldithiocarbamato)tellurium(IV). This points to the weakening in the ligation of the dithiocarbamate group $R_1R_2NCS_2^-$ as the substituents R_1 and R_2 are made electron withdrawing.

Figure 1 gives an ORTEP[11] drawing of the molecule. Five out of the six sulfur atoms in the molecule (S(1) to S(5)) form the equatorial girdle around Te, which is not planar. The chlorine atom and the sixth sulfur atom, S(6), occupy the axial positions in the pentagonal-bipyramidal geometry, the Cl–Te–S(6) angle being 176.4°. The equatorial Te–S bond lengths vary between 2.623 and 2.800 Å and the interbond angles between 66.7 and 71.1°. The axial Te–S length is considerably shorter (2.464 Å) and close to the sum of the covalent radii of Te and S, namely 2.36 Å. The nonplanarity of the equatorial sulfur group is caused by the movement of S(5) out of the equatorial girdle toward the axial sulfur atom S(6), as the bite of the bidentate ligand S(5)–S(6) is too small to subtend an angle of 90° at the center. Figure 2 shows the coordination around Te.

The average Te–S distance of 2.696 Å in TeL_3Cl is less than 2.74 Å, the value found in TeL_4,[12,13] and greater than 2.642 Å in TeL_2I_2,[14] indicating the dependence of Te–S distance on the number of dithiocarbamates around Te. The C–N bond distances in the three ligands agree with published values, and the bond angles at C(1), C(6), C(10), N(1), N(2), and N(3)

Table II. Final Fractional Atomic Coordinates ($\times 10^5$ for Te, Cl, and S Atoms; $\times 10^4$ for Other Atoms; $\times 10^3$ for Hydrogen Atoms) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Te	36825 (4)	31764 (2)	81637 (3)
Cl	60764 (16)	34344 (7)	96102 (11)
S(1)	47854 (17)	23943 (7)	70645 (11)
S(2)	36834 (16)	19551 (8)	87988 (12)
S(3)	29949 (17)	43846 (7)	83494 (13)
S(4)	44482 (16)	39262 (7)	68473 (12)
S(5)	16183 (16)	31235 (8)	92066 (11)
S(6)	15104 (17)	29833 (8)	69699 (12)
O(1)	7305 (4)	724 (2)	9348 (3)
O(2)	4195 (5)	330 (2)	6092 (3)
O(3)	5775 (4)	5901 (2)	9049 (3)
O(4)	3001 (4)	5420 (2)	5182 (3)
O(5)	−1689 (5)	1727 (2)	8515 (3)
O(6)	−1550 (4)	3800 (2)	6209 (3)
Ow(1)	−999 (6)	4385 (2)	8042 (4)
Ow(2)	−2780 (5)	4762 (3)	9226 (4)
N(1)	5066 (4)	1224 (2)	7803 (4)
N(2)	4218 (4)	5146 (2)	7270 (3)
N(3)	−587 (5)	2832 (2)	7802 (4)
C(1)	4572 (6)	1792 (3)	7893 (4)
C(2)	4956 (6)	721 (3)	8549 (5)
C(3)	6019 (6)	790 (2)	9538 (5)
C(4)	5775 (7)	1078 (2)	6986 (4)
C(5)	4849 (6)	909 (3)	5970 (5)
C(6)	3923 (5)	4561 (3)	7463 (4)
C(7)	3743 (6)	5690 (2)	7765 (5)
C(8)	4820 (6)	6162 (3)	8213 (5)
C(9)	4983 (6)	5291 (3)	6495 (4)
C(10)	4213 (6)	5724 (3)	5660 (4)
C(11)	714 (7)	2966 (3)	8001 (4)
C(12)	−1318 (7)	2831 (3)	8635 (5)
C(13)	−1218 (7)	2224 (3)	9208 (5)
C(14)	−1379 (7)	2697 (3)	6754 (5)
C(15)	−2273 (7)	3244 (3)	6323 (5)

atom	bonded to	*x*	*y*	*z*
H(1)	C(2)	510 (5)	36 (2)	833 (4)
H(2)	C(2)	415 (6)	68 (3)	880 (5)
H(3)	C(3)	576 (5)	44 (2)	997 (4)
H(4)	C(3)	593 (6)	120 (3)	985 (5)
H(5)	O(1)	732 (7)	541 (3)	534 (6)
H(6)	C(4)	630 (5)	74 (2)	722 (4)
H(7)	C(4)	624 (5)	143 (3)	683 (4)
H(8)	C(5)	544 (5)	83 (3)	550 (4)
H(9)	C(5)	413 (5)	123 (3)	578 (4)
H(10)	O(2)	855 (6)	469 (3)	52 (5)
H(11)	C(7)	343 (6)	558 (3)	835 (5)
H(12)	C(7)	305 (5)	594 (2)	728 (4)
H(13)	C(8)	70 (5)	153 (2)	666 (4)
H(14)	C(8)	535 (6)	623 (3)	775 (5)
H(15)	O(3)	560 (8)	593 (4)	954 (6)
H(16)	C(9)	524 (5)	490 (2)	618 (4)
H(17)	C(9)	586 (7)	549 (3)	684 (5)
H(18)	C(10)	518 (5)	418 (3)	479 (4)
H(19)	C(10)	596 (4)	388 (2)	405 (4)
H(20)	O(4)	744 (7)	434 (3)	517 (5)
H(21)	C(12)	909 (5)	318 (2)	914 (4)
H(22)	C(12)	774 (5)	292 (2)	834 (4)
H(23)	C(13)	976 (6)	211 (3)	961 (4)
H(24)	C(13)	826 (5)	227 (3)	972 (4)
H(25)	O(5)	815 (6)	142 (3)	882 (5)
H(26)	C(14)	919 (6)	258 (3)	630 (5)
H(27)	C(14)	811 (6)	232 (3)	678 (5)
H(28)	C(15)	721 (5)	311 (2)	562 (4)
H(29)	C(15)	715 (6)	330 (3)	684 (4)
H(30)	O(6)	864 (7)	398 (4)	671 (6)
H(31)	Ow(1)	536 (7)	961 (3)	677 (6)
H(32)	Ow(1)	827 (6)	456 (3)	819 (5)
H(33)	Ow(2)	670 (6)	513 (3)	919 (5)
H(34)	Ow(2)	686 (6)	440 (3)	941 (5)

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Table III. Bond Distances (A) and Bond Angles (deg)

Te–Cl	2.813 (1)	S(3)–C(6)	1.724 (6)
Te–S(1)	2.640 (1)	S(4)–C(6)	1.730 (6)
Te–S(2)	2.729 (2)	C(6)–N(2)	1.318 (7)
Te–S(3)	2.689 (2)	N(2)–C(7)	1.468 (7)
Te–S(4)	2.623 (2)	N(2)–C(9)	1.471 (8)
Te–S(5)	2.800 (1)	C(7)–C(8)	1.513 (8)
Te–S(6)	2.464 (2)	C(9)–C(10)	1.519 (7)
C(8)–O(3)	1.418 (7)	C(10)–O(4)	1.421 (7)
S(1)–C(1)	1.737 (6)	S(5)–C(11)	1.695 (6)
S(2)–C(1)	1.711 (7)	S(6)–C(11)	1.757 (7)
C(1)–N(1)	1.326 (8)	C(11)–N(3)	1.337 (8)
N(1)–C(2)	1.481 (7)	N(3)–C(12)	1.479 (8)
N(1)–C(4)	1.477 (7)	N(3)–C(14)	1.474 (7)
C(2)–C(3)	1.514 (8)	C(12)–C(13)	1.490 (8)
C(4)–C(5)	1.510 (7)	C(14)–C(15)	1.511 (8)
C(3)–O(1)	1.413 (7)	C(13)–O(5)	1.414 (8)
C(5)–O(2)	1.429 (8)	C(15)–O(6)	1.424 (8)

Cl–Te–S(1)	94.6 (1)	S(1)–C(1)–N(1)	120.4 (5)
Cl–Te–S(2)	92.0 (1)	S(2)–C(1)–N(1)	121.8 (4)
Cl–Te–S(3)	87.7 (1)	S(1)–C(1)–S(2)	117.8 (3)
Cl–Te–S(4)	89.3 (1)	C(1)–N(1)–C(2)	120.3 (5)
Cl–Te–S(5)	108.3 (1)	C(1)–N(1)–C(4)	121.5 (5)
Cl–Te–S(6)	176.4 (1)	C(2)–N(1)–C(4)	118.2 (4)
S(1)–Te–S(2)	66.7 (1)	N(1)–C(2)–C(3)	111.2 (6)
S(1)–Te–S(3)	143.9 (1)	N(1)–C(4)–C(5)	113.2 (5)
S(1)–Te–S(4)	77.1 (1)	C(2)–C(3)–O(1)	110.8 (4)
S(1)–Te–S(5)	136.4 (1)	C(4)–C(5)–O(2)	108.7 (4)
S(1)–Te–S(6)	88.9 (1)	S(3)–C(6)–N(2)	121.9 (4)
S(2)–Te–S(3)	149.3 (1)	S(4)–C(6)–N(2)	122.1 (4)
S(2)–Te–S(4)	143.7 (1)	S(3)–C(6)–S(4)	116.1 (3)
S(2)–Te–S(5)	75.7 (1)	C(6)–N(2)–C(7)	122.5 (5)
S(2)–Te–S(6)	88.7 (1)	C(6)–N(2)–C(9)	121.3 (5)
S(3)–Te–S(4)	67.0 (1)	C(7)–N(2)–C(9)	116.0 (4)
S(3)–Te–S(5)	75.3 (1)	N(2)–C(7)–C(8)	114.1 (5)
S(3)–Te–S(6)	89.9 (1)	N(2)–C(9)–C(10)	111.5 (5)
S(4)–Te–S(5)	137.5 (1)	C(7)–C(8)–O(3)	111.4 (5)
S(4)–Te–S(6)	92.2 (1)	C(9)–C(10)–O(4)	108.1 (5)
S(4)–Te–S(6)	92.2 (1)	C(9)–C(10)–O(4)	108.1 (4)
S(5)–Te–S(6)	68.4 (1)	S(5)–C(11)–N(3)	122.5 (5)
S(6)–C(11)–N(3)	118.5 (4)	C(12)–C(13)–O(5)	109.8 (5)
Te–S(1)–C(1)	88.7 (2)	S(5)–C(11)–S(6)	118.9 (4)
Te–S(2)–C(1)	86.3 (2)	C(11)–N(3)–C(12)	120.9 (5)
Te–S(3)–C(6)	86.3 (2)	C(11)–N(3)–C(14)	122.7 (6)
Te–S(4)–C(6)	88.9 (2)	C(12)–N(3)–C(14)	116.4 (5)
Te–S(5)–C(11)	81.5 (2)	N(3)–C(12)–C(13)	113.5 (6)
Te–S(6)–C(11)	91.0 (2)	N(3)–C(14)–C(15)	111.5 (5)
C(14)–C(15)–O(6)	113.0 (5)		

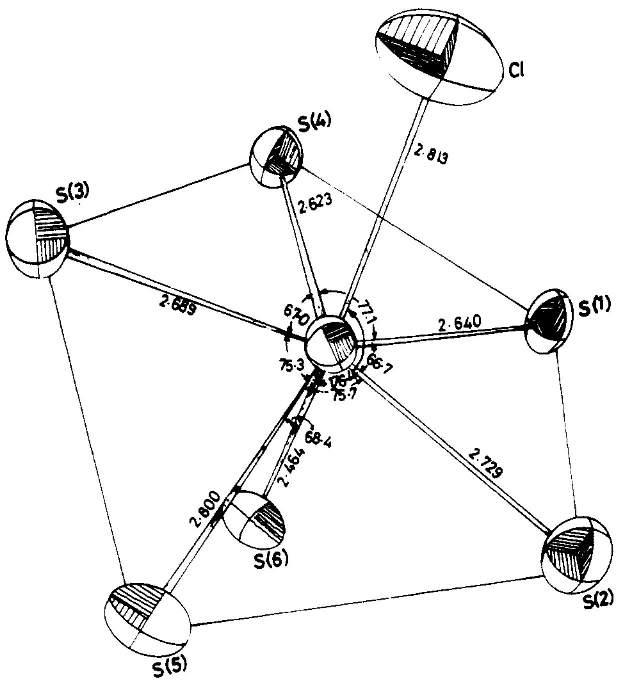

Figure 2. Coordination around the Te atom.

Table IV. Hydrogen-Bond Parameters

D–H- -A[a]	D- -A, Å	D–H, Å	A- -H, Å	D–H- -A, deg
Ow(2)–H(33)- -O(3)	2.882	0.95	1.88	175
O(2″)–H(10)- -Ow(2)	2.835	0.89	1.95	177
Ow(1)–H(32)- -Ow(2)	2.800	0.91	1.98	149
O(6)–H(30)- -Ow(1)	2.683	0.76	1.93	173
O(4′)–H(20)- -O(6)	2.671	0.77	1.91	171
O(1‴)–H(5)- -O(4′)	2.699	0.84	1.89	162
O(5)–H(25)- -O(1)	2.716	0.81	1.93	166
Ow(2)–H(34)- -Cl	3.144	0.91	2.25	169
O(3)–H(15)- -Cl′	3.226	0.73	2.64	139
Ow(1)–H(31‴)- -O(2‴)	2.798	0.81	2.02	161

[a] Symmetry code: (′) $\bar{x}, \bar{y}, \bar{z}$; (″) $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (‴) $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$.

are consistent with sp^2 hybridization of these atoms. Unequal S–C bond distances in each ligand occur along with unequal Te–S bond lengths, suggesting the presence of the canonical forms of the dithiocarbamate group.

Two points merit special mention regarding the structure and reactivity of the complex. First, the Te–Cl bond (2.813 Å) is very much longer than that reported in $TeCl_6^{2-}$ (2.546 Å).[15] The sum of the covalent radii of Te and Cl is 2.31 Å, and the sum of van der Waals radii is 3.81 Å. Therefore, the Te–Cl interaction in TeL_3Cl can be taken as only a weak secondary interaction.[16] Among the three chloro(dithiocarbamato)tellurium(IV) complexes, namely $Te(DEDTC)_3Cl$,[17] $Te(MeMEADTC)_3Cl$,[18] and TeL_3Cl, it is in the present complex that the Te–Cl interaction the weakest. The weakening of the Te–Cl bond is ascribed to the trans effect of the sulfur atom. It is also reflected in the observed ready hydrolysis of the complex (unlike the case of $Te(DEDTC)_4$) on treatment with water and dilute acids. The products of the hydrolysis were identified as TeL_3OH and TeO^{2+}. We have also observed increasing stability toward hydrolysis of the halo(dithiocarbamato)tellurium(IV) complexes on changing the halides in the order Cl^-, Br^-, and I^-. This change involves increasing covalent interaction between the halides and the metal ion. Second, it is difficult to suggest any stereochemical significance to the lone pair of electrons in Te(IV) in this complex due to the highly distorted and varying strengths of interaction of the mixed-ligand complex. It is significant to point out that in Te(IV) chemistry, the lone pair seems to exert little influence even in simpler cases such as in $TeCl_6^{2-}$.[15]

The chlorine atom and all the oxygen atoms participate in hydrogen bonding. The relevant bonding parameters are given in Table IV. Each ethanol oxygen forms one intermolecular and two intramolecular bondings except O(5), which is involved only in intramolecular bonding. The water oxygen Ow(1) is surrounded by three hydrogen atoms, the interbond angles around it being 110, 113, and 121°. The other water oxygen Ow(2) has four hydrogen atoms around it. The Ow(1)–H(32)- -Ow(2) angle of 149° shows large deviation from linearity. The chlorine atom forms two intermolecular hydrogen bonds, the O–H- -Cl angles being 169 and 139°. The packing arrangement seems to be mainly dictated by the hydrogen-bonding network. The hydrogen-bonding scheme in the molecule and a packing diagram in the unit cell of TeL_3Cl have been deposited as supplementary material.

The observed coordination around Te in TeL_3Cl agrees with one of the three geometries predicted by Kepert[19] from minimum energy calculations for structures of the type M[(bi-

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dentate)$_3$(unidentate)], namely a configuration between that of a pentagonal bipyramid and a capped trigonal prism.

Registry No. TeO_2, 7446-07-3; $TeCl[(HOC_2H_4)_2NCSS]_3 \cdot 2H_2O$, 86455-82-5; diethyldithiocarbamic acid, 147-84-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and structure factor amplitudes and Figures 3 and 4, depicting the hydrogen bonding in the molecule and packing in the unit cell (15 pages). Ordering information is given on any current masthead page.

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Synthesis and the Crystal and Molecular Structure of a Platinum-Bridged Derivative of Roussin's Red Salt, $(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(NO)_4$[1]

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The reaction of Roussin's red salt $Na_2[Fe_2(\mu\text{-}S)_2(NO)_4]$ and *cis*-$(Ph_3P)_2PtCl_2$ in THF yields $(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(NO)_4$. This compound also can be synthesized through the displacement of CO by NO from $(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(CO)_6$ in solution. $(Ph_3P)_2Pt(\mu_3\text{-}S)_2Fe_2(NO)_4$ crystallizes in the monoclinic space group $C2/c$ (C_{2h}^6; No. 15) with $a = 20.867$ (7) Å, $b = 19.616$ (6) Å, $c = 20.524$ (4) Å, $\beta = 113.18$ (2)°, $V = 7723$ (3) Å^3, and $Z = 8$. Full-matrix least-squares refinement provided a final R value of 0.060 based on 3790 independent reflections. The planar S_2Fe_2 rhombus of Roussin's red salt is folded in the platinum adduct, and both linear and substantially bent nitrosyl ligands are present on each Fe atom.

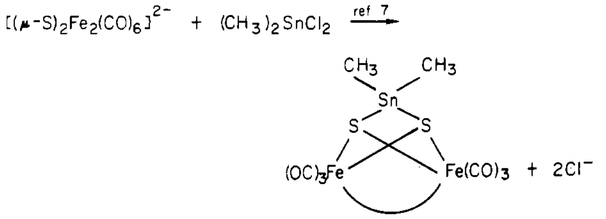
Introduction

Although Roussin's red salt was first reported in 1858,[3] its constitution and structure remained unknown for some time. In 1882, Pavel[4] correctly reported the composition of its potassium salt to be "$Fe(NO)_2SK + 2H_2O$". A dimeric constitution, "$Fe(NO)_2S$, $Fe(NO)_2$, and K_2S", was suggested.[4] Although the structure of the diethyl derivative, obtained by reaction of Roussin's red salt with iodoethane,[2] was determined in 1958 by Thomas et al.,[5] the structure of a salt of the $Fe_2S_2(NO)_4^{2-}$ anion was not reported until 1981.[6]

Both the diethyl derivative, $(\mu\text{-}C_2H_5S)_2Fe_2(NO)_4$, and the $S_2Fe_2(NO)_4^{2-}$ anion contain a planar Fe_2S_2 rhombus. Noteworthy is the large distance between S atoms in the Fe_2S_2 unit: 3.633 Å in the diethyl derivative[5] and 3.575 Å in anion.[6]

In earlier work, the seemingly related $Fe_2S_2(CO)_6^{2-}$ anion had been prepared by reaction of $Fe_2(\mu\text{-}S)_2(CO)_6$ with 2 molar equiv of $LiBEt_3H$ in THF at −78 °C.[7] Although the structure of a salt of this anion has not been reported to date, the crystal structure of its diethyl derivative, $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$, showed that a puckered Fe_2S_2 core unit is present, with a S···S distance of 2.932 Å.[8] It may be expected that the S···S distance in the $S_2Fe_2(CO)_6^{2-}$ anion will only be slightly greater than that found for $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$.

The proximity of the two sulfur atoms in these sulfur-ligand-bridged $Fe_2(CO)_6$ complexes has allowed the preparation of many $Fe_2(CO)_6$ species that contain diverse organic group, metalloid, and metal bridges between the sulfur atoms. The reactions in eq 1 and 2 are illustrative. Transition-metal derivatives such as the bis(triphenylphosphine)platinum(II) compound **1** were also prepared, by the reaction of either $(\mu\text{-}S)_2Fe_2(CO)_6^{2-}$ with $(Ph_3P)_2PtCl_2$[7] or $(\mu\text{-}S)_2Fe_2(CO)_6$ with $(Ph_3P)_4Pt$.[10]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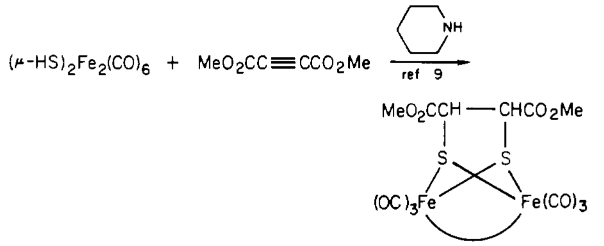
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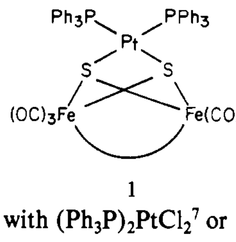
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