

## Synthesis, Stereochemistry, and Mechanism of Formation of Mixed Bis(dithiolato)nickel Dimers

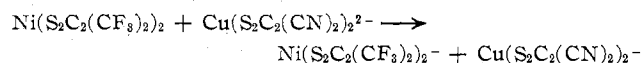
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Received October 14, 1971

Bis(*cis*-1,2-perfluoromethylene-1,2-dithiolato)nickel, nickel dithiete, reacts with several 1,1-dithiolates to produce centrosymmetric mixed-ligand dimers of nickel. Kinetic measurements at room temperature along with spectroscopic and conductivity measurements at low temperatures (*e.g.*,  $-80^{\circ}$ ) indicate the rapid and reversible formation of a polarized 1:1 intermediate between nickel dithiete and metal bis(1,1-dithiolates). A singular exception, copper bis(dithiocarbamate), leads under all reaction conditions studied by us to the instantaneous formation of a 1:1 salt. At room temperature all systems ultimately yield the mixed-ligand dimer (*vide supra*) as the sole nickel-containing product. Xanthates react much more slowly than dithiocarbamates with the influence of the metal being, in decreasing order of rates: nickel, zinc, copper. The structure of the nickel thiete diethyldithiocarbamate dimer was established by a single-crystal X-ray diffraction study. The crystals studied belong to space group  $P\bar{1}$  with  $a = 7.793$  (3),  $b = 12.880$  (7),  $c = 9.624$  (6) Å,  $\alpha = 61.07$  (4),  $\beta = 111.38$  (2), and  $\gamma = 108.03$  (4) $^{\circ}$ , with the observed density being 1.87 g/cm $^3$  as compared to 1.86 g/cm $^3$  required for one formula unit per unit cell. Least-squares refinement of 1762 counter-collected unique reflections having  $|F|^2 > 3\sigma(|F|^2)$  led to a final value of the conventional  $R$  factor (on  $F$ ) of 0.052. The structure consists of well-separated centrosymmetric sulfur-bridged dimers with the nickel ion having a square-pyramidal coordination stereochemistry and lying 0.36 Å out of the equatorial plane in the direction of the apical bridge sulfur. The two bridging sulfur atoms are provided by the thiete ligands (one from each) which in turn have structural features representative of reduced ligand (*e.g.*, localized C-C double bonds, 1.36 Å). Nickel-sulfur distances are respectively 2.156 (2) Å for thiete (tfd), 2.234 (2) Å for carbamate (dte), and 2.428 (2) Å for the bridge bonds.

### Introduction

Since their discovery,<sup>1</sup> complexes of the type  $M_m-[S_2C_2R_2]_n$  ( $M =$  a transition metal;  $R =$  alkyl, aryl, cyano, perfluoromethyl;  $m = 1, 2$ ;  $n = 2, 3, 4$ ) have been the subject of numerous investigations,<sup>2-4</sup> most of which have dealt chiefly with their synthesis, structure, and magnetic properties. Much of the work revolved around the reversible electron-transfer properties of these complexes which subsequently led to their utilization as oxidizing agents<sup>5</sup> in the synthesis of new electron-transfer series, *e.g.*



These syntheses assumed that "scrambling" or ligand exchange either did not occur or was negligibly slow.

Subsequently, however, polarographic investigations of both the planar nickel and the square-pyramidal nitrosyl iron bis(dithiolenes) have shown that ligand reorganization does occur slowly under suitable conditions.<sup>6,7</sup> More recently, studies of the cobalt and iron bis(dithiolenes),  $(Co(S_2C_2(CF_3)_2)_2)_2$  and  $(Fe(S_2C_2(CF_3)_2)_2)_2$ , have shown exchange reactions to occur between dimeric bis(dithiolenes) as well.<sup>8</sup> van der Linden and van der Roer have taken advantage of a ligand-exchange reaction to prepare mixed dithiomalonitrile-dithiocarbamate complexes of nickel.<sup>9</sup>

Here we present the results of our work on the very rapid exchange of the dithiolene  $Ni(S_2C_2(CF_3)_2)_2$ , **1**,

(1) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **84**, 3221 (1962).

(2) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(3) D. Cocouvanis, *ibid.*, **11**, 233 (1970).

(4) R. Eisenberg, *ibid.*, **12**, 295 (1970).

(5) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

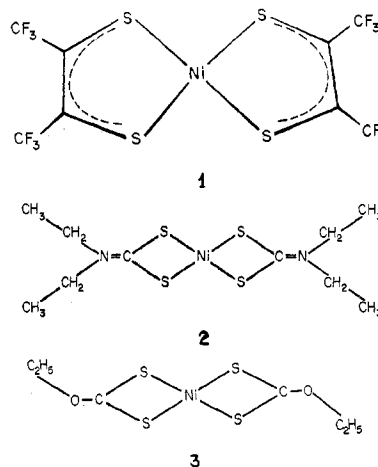
(6) A. Davison, J. A. McCleverty, E. T. Shawl, and E. J. Wharton, *J. Amer. Chem. Soc.*, **89**, 830 (1967).

(7) E. J. Wharton, C. J. Winscom, and J. A. McCleverty, *Inorg. Chem.*, **8**, 303 (1969).

(8) A. L. Balch, *ibid.*, **10**, 388 (1971).

(9) J. G. M. van der Linden and H. G. J. van der Roer, *Inorg. Chim. Acta*, **5**, 254 (1971).

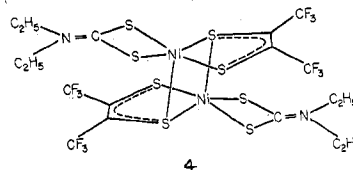
with nickel bis(diethyldithiocarbamate), **2**, and nickel bis(ethyl xanthate), **3**. The present report emphasizes the synthesis, mechanism of formation in noncoordinating solvents, and structural chemistry of the mixed-ligand dimers obtained.



### Results and Discussion

**Synthesis and Properties.**—Mixed dithiolate ligand dimers, **4** and **5**, are readily prepared by reaction of nickel dithiete, **1**, with the appropriate nickel bis(1,1-dithiolate), **2** or **3**, at room temperature. Both compounds are crystalline, air-stable, diamagnetic, intensely green solids which are soluble in aromatic and most halogenated hydrocarbon solvents.

Both compounds are quite sensitive toward a variety of Lewis bases (*e.g.*, acetonitrile, DMF, DMSO, triphenylphosphine, etc.), decomposing to give bright



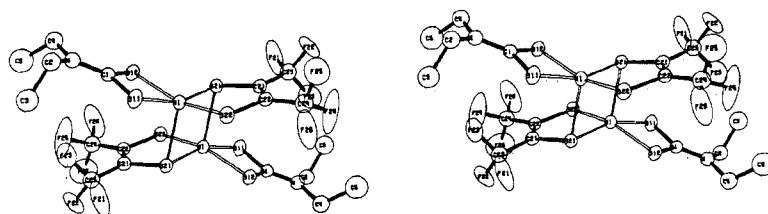


Figure 1.—A perspective view of the mixed dithiolate ligand dimer of nickel. These drawings constitute a stereopair which may be best seen with the aid of a hand viewer.

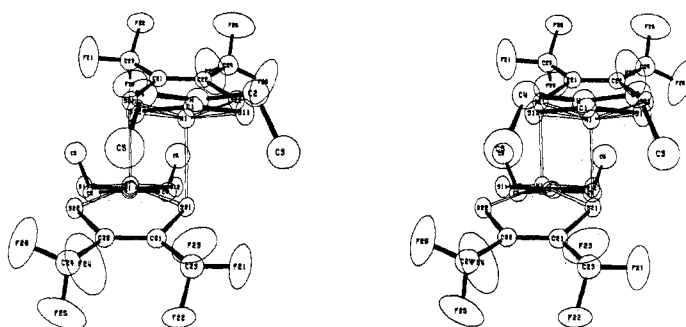
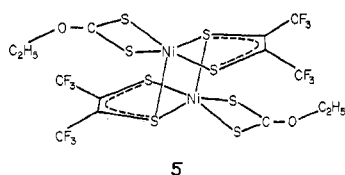


Figure 2.—A view of the dimer which emphasizes the nonplanarity of the Ni-S<sub>4</sub> monomer unit.



yellow solutions containing the easily identifiable monoanion of **1**.

Chemical reduction can be achieved using an acetone solution of *o*-phenylenediamine to yield canary yellow solutions containing the ions **4**<sup>2-</sup> or **5**<sup>2-</sup> or more likely the corresponding monomer monoanions. Confirmation of the two-electron reduction has been made by titrimetry as well as by cyclic voltammetry using **1** as an internal calibrant. The difference in the reduction potentials, +0.29 and +0.46 V for **4** and **5**, respectively, probably reflects the difference in inductive effects of the substituents -NEt<sub>2</sub> and -OEt.

Formation of **4** also occurs in the reactions of **1** with a variety of metal diethyldithiocarbamates (*e.g.*, Co(Et<sub>2</sub>dtc)<sub>3</sub>, Pd(Et<sub>2</sub>dtc)<sub>2</sub>, Pt(Et<sub>2</sub>dtc)<sub>2</sub>, Cu(Et<sub>2</sub>dtc)<sub>2</sub>, and Zn(Et<sub>2</sub>dtc)<sub>2</sub>). In addition to **4**, these reactions yield a number of other products whose isolation and characterization is currently in progress.<sup>10</sup>

Significantly, **4** could not be obtained from NaEt<sub>2</sub>dtc and **1**<sup>-</sup>, even at reflux in acetone for days. This, together with the fact that **4** is obtained from **1**<sup>-</sup> and Cu(Et<sub>2</sub>dtc)<sub>2</sub><sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>, suggests that a charge-separated intermediate involving **1** and **2** or **1** and **3** may play a role in the formation of **4** and **5**. Further evidence for the existence and nature of such an intermediate and speculation on the reaction mechanism will be taken up later.

**Molecular and Electronic Structure.**—As shown in Figures 1 and 2, the structure of the complex<sup>11</sup> is a

(10) These products appear to be the same as those obtained by direct reaction of metal dithiocarbamates with free 1,2-dithiolenes (*e.g.*, Cu(dtc)-(tfd) has been isolated and characterized), but the yields appear to be much better: ref 9; L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971).

centrosymmetric mixed-ligand dimer in which the nickel atoms occupy a square-pyramidal environment. Dimerization occurs through the sharing of thiete ligand sulfur atoms, with the bridging sulfurs occupying the apical sites of identical square pyramids. Little direct metal-metal interaction is indicated since the molecular Ni-Ni distance is 2.955 (2) Å.<sup>12</sup> The Ni atom is displaced 0.36 Å out of the best plane (Table IV) of the four basal sulfurs in the direction of the bridging sulfur atoms. Although the thiete and dithiocarbamate ligands are very nearly planar, they are displaced from the basal sulfur plane as well, with the thiete ligand being the further removed due to the participation of sulfur atom S<sub>21</sub> in the bridging ring (Figures 1, 2). The ligands of each half-dimer are inclined at an angle of about 34° to each other. Each half-dimer moiety is therefore continuously curved so that it is somewhat bowl shaped in appearance.

The metal-sulfur distances vary significantly with the nickel-sulfur bridging bond distance being *ca.* 0.3 Å longer than the in-plane thiete sulfur-nickel distances. Nevertheless, this clearly represents a considerable interaction which is confirmed by the large displacement of the nickel atom from the S<sub>4</sub> basal plane.

Within a monomer unit, the thiete sulfur-nickel distances are about 0.1 Å shorter than the dithiocarbamate sulfur-nickel distances which is consistent with the strong  $\pi$ -acid nature of the thiete ligand. The marginal difference between the in-plane thiete sulfur-metal distances is not unexpected, in view of their different chemical environments. Except for a small increase in the nickel-sulfur distances, the dithiocarbamate ligand bond lengths are essentially unchanged from their values in nickel bis(diethyldithiocarbamate)<sup>13</sup> (Table V).

(11) Structural parameters of interest are tabulated in the Experimental Section of this paper; *vide infra*.

(12) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 256.

(13) M. Bonamico, G. Dessy, C. Mariani, A. Vacicgo, and L. Zambonelli, *Acta Crystallogr.*, **19**, 619 (1965).

TABLE I  
 POSITIONAL AND THERMAL PARAMETERS IN  $[\text{Ni}(\text{dte})(\text{tfd})]_2^a$ 

Atom	$x^b$	$y$	$z$	$\beta_{11}^c$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ni	0.0507 (9)	0.0023 (10)	0.1622 (10)	122 (2)	56 (1)	99 (2)	8 (1)	31 (2)	-25 (1)
S <sub>11</sub>	0.1089 (19)	-0.1123 (22)	0.4326 (20)	136 (5)	85 (2)	104 (4)	14 (3)	25 (3)	-22 (2)
S <sub>12</sub>	-0.2320 (18)	-0.0506 (20)	0.2075 (20)	135 (5)	75 (2)	106 (3)	22 (2)	32 (3)	-24 (2)
S <sub>21</sub>	-0.0367 (17)	0.1473 (19)	-0.0720 (19)	121 (4)	56 (2)	109 (3)	17 (2)	24 (3)	-24 (2)
S <sub>22</sub>	0.3405 (18)	0.0821 (20)	0.1762 (20)	126 (5)	67 (2)	117 (4)	14 (2)	18 (3)	-28 (2)
C <sub>1</sub>	-0.124 (7)	-0.127 (7)	0.410 (7)	2.9 (1)					
N	-0.210 (6)	-0.189 (6)	0.529 (7)	3.5 (1)					
C <sub>2</sub>	-0.100 (9)	-0.247 (9)	0.701 (9)	4.4 (2)					
C <sub>3</sub>	-0.078 (13)	-0.371 (13)	0.746 (13)	6.5 (3)					
C <sub>4</sub>	-0.413 (10)	-0.194 (11)	0.496 (11)	4.9 (2)					
C <sub>5</sub>	-0.539 (21)	-0.315 (22)	0.510 (24)	9.0 (4)					
C <sub>21</sub>	0.169 (7)	0.249 (7)	-0.101 (8)	3.2 (2)					
C <sub>22</sub>	0.335 (7)	0.218 (7)	0.008 (7)	3.0 (2)					
C <sub>23</sub>	0.145 (8)	0.366 (9)	-0.247 (9)	4.4 (2)					
C <sub>24</sub>	0.522 (9)	0.292 (9)	-0.003 (9)	4.7 (2)					
F <sub>21</sub>	-0.031 (6)	0.380 (6)	-0.317 (8)	277 (18)	106 (7)	405 (19)	9 (9)	-40 (15)	81 (9)
F <sub>22</sub>	0.225 (6)	0.459 (5)	-0.214 (6)	473 (22)	54 (5)	310 (15)	2 (8)	65 (15)	-67 (7)
F <sub>23</sub>	0.210 (9)	0.381 (7)	-0.365 (7)	873 (40)	119 (8)	231 (14)	99 (14)	264 (20)	21 (8)
F <sub>24</sub>	0.540 (7)	0.358 (11)	-0.149 (9)	338 (23)	372 (18)	389 (22)	-171 (16)	196 (19)	-65 (17)
F <sub>25</sub>	0.560 (7)	0.372 (9)	0.048 (12)	420 (26)	288 (15)	986 (26)	-200 (16)	350 (28)	-434 (24)
F <sub>26</sub>	0.655 (6)	0.236 (7)	0.068 (11)	163 (16)	134 (9)	925 (39)	8 (9)	163 (20)	21 (15)

<sup>a</sup> dte = diethyldithiocarbamate and tfd = bis(*cis*-1,2-perfluoromethylethene)-1,2-dithiolate in this and succeeding tables. <sup>b</sup> Estimated errors of last significant figures are given in parentheses. <sup>c</sup> The units of the isotropic thermal parameters are Å<sup>2</sup>. The form of the anisotropic thermal ellipsoid is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ , and the  $\beta$  values have been scaled times 10<sup>4</sup>.

 TABLE II  
 PRINCIPAL INTRAMOLECULAR BOND LENGTHS (Å)  
 IN  $[\text{Ni}(\text{dte})(\text{tfd})]_2^a$ 

Ni-S <sub>11</sub>	2.234 (2)	C <sub>1</sub> -N	1.32 (1)
Ni-S <sub>12</sub>	2.234 (2)	N-C <sub>2</sub>	1.48 (1)
Ni-S <sub>21</sub>	2.152 (2)	N-C <sub>4</sub>	1.48 (1)
Ni-S <sub>22</sub>	2.156 (2)	C <sub>2</sub> -C <sub>3</sub>	1.49 (1)
Ni*-S <sub>21</sub> <sup>b</sup>	2.428 (2)	C <sub>4</sub> -C <sub>5</sub>	1.54 (1)
S <sub>11</sub> -C <sub>1</sub>	1.71 (1)	C <sub>23</sub> -F <sub>21</sub>	1.31 (1)
S <sub>12</sub> -C <sub>1</sub>	1.71 (1)	C <sub>23</sub> -F <sub>22</sub>	1.30 (1)
S <sub>21</sub> -C <sub>21</sub>	1.74 (1)	C <sub>23</sub> -F <sub>23</sub>	1.31 (1)
S <sub>22</sub> -C <sub>22</sub>	1.72 (1)	C <sub>24</sub> -F <sub>24</sub>	1.28 (1)
C <sub>21</sub> -C <sub>22</sub>	1.36 (1)	C <sub>24</sub> -F <sub>25</sub>	1.26 (1)
C <sub>21</sub> -C <sub>23</sub>	1.49 (1)	C <sub>24</sub> -F <sub>26</sub>	1.24 (1)
C <sub>22</sub> -C <sub>24</sub>	1.49 (1)	$\langle \text{C}_{23}\text{-F} \rangle$	1.31 (1)
		$\langle \text{C}_{24}\text{-F} \rangle$	1.26 (1)

<sup>a</sup> The numbers in parentheses are the estimated standard deviations in the last significant digits. <sup>b</sup> The asterisk refers to the centrosymmetrically related position.

 TABLE III  
 SELECTED INTRAMOLECULAR BOND ANGLES (DEG)  
 IN  $[\text{Ni}(\text{dte})(\text{tfd})]_2$ 

S <sub>11</sub> -Ni-S <sub>12</sub>	77.52 (7)	C <sub>1</sub> -N-C <sub>2</sub>	120.0 (6)
S <sub>12</sub> -Ni-S <sub>21</sub>	92.28 (7)	C <sub>1</sub> -N-C <sub>4</sub>	120.8 (7)
S <sub>22</sub> -Ni-S <sub>21</sub>	91.47 (7)	C <sub>2</sub> -N-C <sub>4</sub>	119.1 (6)
S <sub>22</sub> -Ni-S <sub>11</sub>	92.65 (7)	N-C <sub>2</sub> -C <sub>3</sub>	112.8 (7)
Ni-S <sub>21</sub> -*Ni	80.10 (6)	N-C <sub>4</sub> -C <sub>5</sub>	116.8 (10)
S <sub>21</sub> -Ni-*S <sub>21</sub>	99.90 (7)	C <sub>21</sub> -C <sub>22</sub> -C <sub>24</sub>	126.1 (6)
Ni-S <sub>11</sub> -C <sub>1</sub>	86.3 (2)	C <sub>22</sub> -C <sub>21</sub> -C <sub>23</sub>	125.3 (6)
Ni-S <sub>12</sub> -C <sub>1</sub>	86.4 (2)	C <sub>21</sub> -C <sub>23</sub> -F <sub>21</sub>	112.7 (6)
Ni-S <sub>21</sub> -C <sub>21</sub>	104.0 (2)	C <sub>21</sub> -C <sub>23</sub> -F <sub>22</sub>	113.4 (6)
Ni-S <sub>22</sub> -C <sub>22</sub>	104.3 (2)	C <sub>21</sub> -C <sub>23</sub> -F <sub>23</sub>	113.6 (6)
S <sub>11</sub> -C <sub>1</sub> -S <sub>12</sub>	109.8 (3)	C <sub>22</sub> -C <sub>24</sub> -F <sub>24</sub>	114.6 (7)
S <sub>21</sub> -C <sub>21</sub> -C <sub>22</sub>	119.5 (5)	C <sub>22</sub> -C <sub>24</sub> -F <sub>25</sub>	112.9 (7)
S <sub>22</sub> -C <sub>22</sub> -C <sub>24</sub>	120.2 (5)	C <sub>22</sub> -C <sub>24</sub> -F <sub>26</sub>	115.8 (7)
S <sub>11</sub> -C <sub>1</sub> -N	125.2 (5)		
S <sub>12</sub> -C <sub>1</sub> -N	125.0 (5)		
S <sub>21</sub> -C <sub>21</sub> -C <sub>23</sub>	115.2 (5)		
S <sub>22</sub> -C <sub>22</sub> -C <sub>24</sub>	113.6 (5)		

Comparison of the relevant bond distances in **1** and **4** reveals that although the thiete sulfur-nickel and carbon-sulfur distances increase in **4**, the dimer carbon-carbon double bond is some 0.02 Å shorter. Similar

 TABLE IV  
 SEVERAL BEST LEAST-SQUARES PLANES IN  $[\text{Ni}(\text{dte})(\text{tfd})]_2^a$ 

Atom	Wt	Distance from plane, Å	Atom	Wt	Distance from plane, Å
Plane 1					
S <sub>11</sub>	32	-0.009	S <sub>21</sub>	32	-0.002
S <sub>12</sub>	32	0.008	S <sub>22</sub>	32	0.003
S <sub>21</sub>	32	-0.006	C <sub>21</sub>	12	0.010
S <sub>22</sub>	32	0.007	C <sub>22</sub>	12	-0.012
Ni	0	-0.356	C <sub>23</sub>	12	0.059
$-0.0221x + 0.9503y + 0.3105z = -1.3948$					
Plane 2					
S <sub>11</sub>	32	-0.001	Ni	0	0.174
S <sub>12</sub>	32	0.001	$-0.2596x + 0.8073y + 0.5299z = 1.0539$		
C <sub>1</sub>	12	-0.004	Plane 4		
N	14	-0.024	Ni	59	0.000
C <sub>2</sub>	12	0.032	S <sub>21</sub>	32	0.000
C <sub>4</sub>	12	-0.000	*Ni	59	0.000
Ni	0	0.049	*S <sub>21</sub>	32	0.000
$0.1414x + 0.9791y + 0.0442z = 0$					
$0.1465z = 0.7956$					

<sup>a</sup> Orthogonal coordinate system with  $y$  parallel to  $b_0$  and  $z$  parallel to  $c_0^*$ .

changes have been found to occur upon reduction of the monoanion of bis(*cis*-1,2-cyanoethene-1,2-dithiolato)-nickel. These changes have been interpreted as consistent with the addition of electron density to a molecular orbital which is metal-sulfur and sulfur-carbon antibonding and carbon-carbon bonding.<sup>14</sup> Thus the structural data indicate that formation of **4** also leads to reduction of the thiete ligands.

An interesting insight into the probable electronic structure of **4** is afforded by comparison with cobalt dithiete.<sup>15</sup> The average basal metal-sulfur bond in cobalt dithiete is 2.161 (4) Å compared to 2.152 (2) Å for the square-pyramidal mixed-ligand complex, **4**. Assuming this difference to be essentially a reflection of the smaller covalent radius of nickel leads to an estimated value of *ca.* 2.37 Å for a bridging nickel-

(14) See ref 3, p 307, and references therein.

(15) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

TABLE V  
 BOND LENGTHS (Å) FOR A REPRESENTATIVE GROUP OF METAL DITHIOLATES

Complex	M—S(tfd)	M—S(dtc)	M—S(bridge)	C—S(tfd)	C—S(dtc)	C=C(tfd)
(Ni(tfd) <sub>2</sub> ) <sub>2</sub> <sup>a</sup>	2.122 (3)	...	...	1.71 (1)	...	1.38 (2)
(Ni(dtc) <sub>2</sub> ) <sub>2</sub> <sup>b</sup>	...	2.201 (2)	...	...	1.706 (7)	...
Ni(tfd) <sub>2</sub> ·NBD <sup>c</sup>	2.149 (4)	...	...	1.78 (1)	...	1.34 (2)
Ni(tfd) <sub>2</sub> ·butadiene <sup>d</sup>	2.157 (7)	...	...	1.77 (2)	...	1.35 (3)
(Ni(dtc)(tfd)) <sub>2</sub> <sup>e</sup>	2.152 (2)	2.234 (2)	2.428 (2)	1.74 (1)	1.71 (1)	1.36 (1)
(Co(tfd) <sub>2</sub> ) <sub>2</sub> <sup>f</sup>	2.161 (6)	...	2.382 (4)	1.72 (2)	...	1.39 (2)

<sup>a</sup> R. D. Schmitt, R. M. Wing, and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 4394 (1969). <sup>b</sup> Reference 13. <sup>c</sup> R. M. Wing, G. C. Tustin, and W. H. Okamura, *J. Amer. Chem. Soc.*, **92**, 1935 (1970). <sup>d</sup> Unpublished results. <sup>e</sup> This work. <sup>f</sup> Reference 15.

sulfur distance in a neutral dimeric nickel dithiete complex. Since this is significantly shorter than the observed apical nickel-sulfur distance (2.428 (2) Å) in **4**, we feel that this is indicative of a half-occupied apical sulfur-nickel antibonding orbital. This conclusion is in agreement with simple ligand field considerations which for a low-spin square-pyramidal Ni(III) complex predict that the highest occupied orbital is an apical sulfur-metal antibonding combination. Thus the difference in the observed and calculated apical nickel-sulfur distances supports the formulation of the metal atom as a d<sup>7</sup> Ni(III) ion. The proposed antibonding nature of the highest occupied orbital is the basis for our suggestion (*vide supra*) that the two-electron reduction observed for **4** leads to mixed-ligand monomer mononion.

The unexpected tucking of the ethyl groups (Figure 2) is apparently a consequence of crystal packing since no interatomic distance indicative of hydrogen bonding to the perfluoromethyl fluorines could be found.<sup>16</sup> All intermolecular contacts were outside the accepted van der Waals limits.

The chemical and physical properties of **5** indicate that its structure is analogous to that of **4** (see, *e.g.*, their spectra, Figure 3).

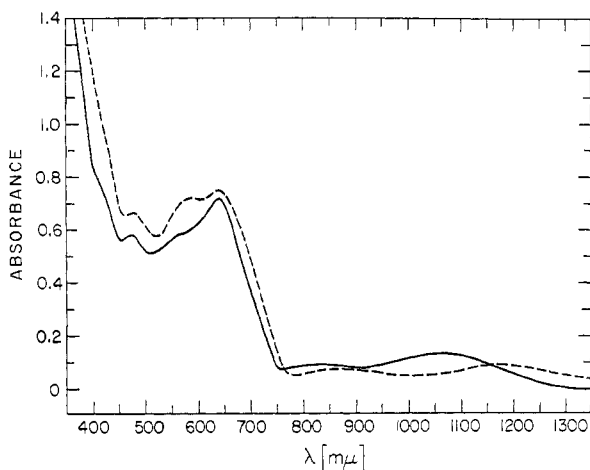


Figure 3.—Near-ir-visible spectra of the mixed-ligand dimers; see text for details: —, compound **5**; ----, compound **4**.

**Reaction Mechanism.**—The room-temperature reaction between **1** and **2** (benzene, toluene, carbon tetrachloride, and dichloromethane solvents) obeys a second-order rate law, first order in each reactant, with a single isosbestic point being observed at 659 nm over a period of *ca.* 4 half-lives.

At *ca.* -60° in place of **4**, the instantaneous forma-

(16) See ref 12, p 464. Also, the CH stretching frequencies are normal and the CH<sub>3</sub> proton resonances occur at the usual field.

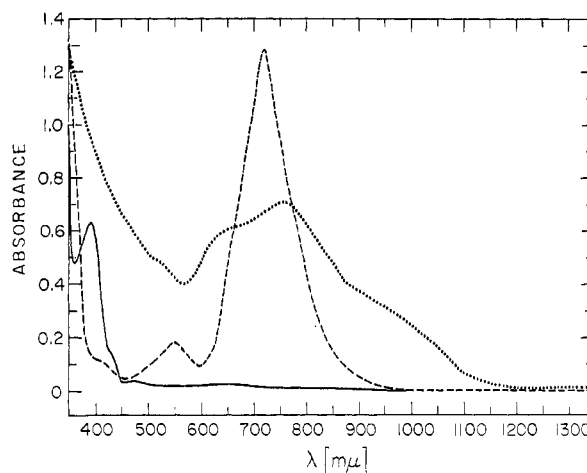
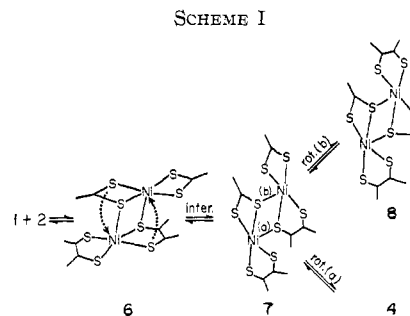


Figure 4.—Near-ir-visible spectrum of the intermediate formed between nickel dithiete and nickel bis(diethyldithiocarbamate) at -60°: ····, intermediate; ----, nickel dithiete; —, nickel bis(diethyldithiocarbamate).

tion of a new species is observed (Figure 4). A Job variational plot<sup>17</sup> at this low temperature clearly shows the new species to be a 1:1 adduct of **1** and **2**. Evidence for the room-temperature existence of this species was provided by the extreme broadening of the long-wavelength side of the nickel dithiete 720-nm band, invariably observed during kinetic runs. Thus we conclude that this material which forms nonconducting solutions at low temperatures is in thermal equilibrium with **1** and **2** and is an intermediate in the reaction mechanism leading to **4**.

A reaction scheme consistent with our observations is shown in Scheme I, which contains as the second step a



ligand-interchange process also proposed by Balch<sup>8</sup> as a step in the ligand-exchange reactions of metal bis-(dithiolene) dimers.

Since we require the interchange to be the rate-determining step in order simultaneously to explain the observed rate law as well as the rapid formation of the

(17) P. Job, *C. R. Acad. Sci.*, **180**, 928 (1925).

adduct between 1 and 2 at low temperature, 6 must be proposed as the intermediate. Indeed this species fits the low-temperature observations quite well, its spectrum mimicking that of the established sulfur-bridged dimer, 4. Also the 700–800-nm region resembles a red-shifted nickel thiete  $b_{2g} \leftarrow b_{1u}$  transition. Such a shift in the absorption to a position lying between the 720-nm band characteristic of 1 and the 800-nm band characteristic of 1<sup>18</sup> might well be expected if the powerful oxidant 1 accepted electron density from 2 to give a highly polarized, although not ionic, species.<sup>19</sup>

The overall mechanism, then, is a rapid preequilibrium to give a steady-state concentration of 6, which rearranges in the rate-determining step to 7, followed by rapid rotation about a nickel-sulfur bridge band (rot. (a)) to give 4. Product 8 (rot. (b)) has never been observed among any of our reaction products, presumably because of the poor donor ability expected for coordinated dithiocarbamate or xanthate sulfur atoms compared to that of the reduced thiete ligand.

### Summary and Conclusion

Reactions of nickel dithiete with a variety of metal dithiocarbamates and xanthates lead to mixed-ligand dimers of nickel. These reactions appear to proceed *via* either a preliminary redox process or formation of a highly polarized donor-acceptor complex, depending on the relative electrode potentials of the reactants. Consistent with the redox character of the reaction, the final product has structural parameters indicative of reduced thiete ligand.

### Experimental Section

Reagent grade sodium diethyldithiocarbamate (Matheson Coleman and Bell) was used without further purification. All solvents were reagent grade and were dried over Linde Type 4A Molecular Sieves before use.

Metal dithiocarbamates and xanthates were prepared according to published procedures,<sup>20</sup> and recrystallizations from dichloromethane were repeated until the crystals were anhydrous. Nickel dithiete, 1, was prepared according to the method of Davison, *et al.*,<sup>5</sup> and recrystallized twice from *n*-pentane to give dark purple platelets.

Analytical data are the results of microanalysis by C. F. Geiger, Ontario, Calif.

$[\text{Ni}\{\text{S}_2\text{C}_2(\text{CF}_3)_2\}\{\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_2]$ .—Nickel bis(diethyldithiocarbamate) (35.5 mg, 0.1 mmol) in 25 ml of  $\text{CH}_2\text{Cl}_2$  was added to a stirred solution of nickel dithiete (51.1 mg, 0.1 mmol) also in 25 ml of  $\text{CH}_2\text{Cl}_2$ . The solution immediately turned an intense forest green. Slow evaporation of the solvent gave lustrous black rhombohedra which were washed with  $\text{CH}_2\text{Cl}_2$  (two 50-ml portions) to give 84.5 mg (98% yield) of product, mp 269.5–270.5° dec. *Anal.* Calcd for  $\text{C}_{18}\text{H}_{20}\text{F}_{12}\text{N}_2\text{S}_8\text{Ni}_2$ : C, 24.96, H, 2.33. Found: C, 25.31; H, 2.38.

The identical product was formed at slower rates in ca. 50% yield (*i.e.*, all nickel incorporated) when the Cu, Zn, Co, Pd, or Pt complex of bis(diethyldithiocarbamate) was used. The xanthate, 5, prepared by the same method was characterized by satisfactory analysis and spectra.

$[\text{Cu}\{\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_2][\text{Ni}\{\text{S}_2\text{C}_2(\text{CF}_3)_2\}_2]$ .—A solution of nickel dithiete (51.1 mg, 0.1 mmol) in 10 ml of  $\text{CH}_2\text{Cl}_2$  was added to a

stirred solution of  $\text{Cu}\{\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2\}_2$  (36 mg, 0.1 mmol) in 15 ml of the same solvent. The color changed immediately from dark brown to an intense dark green. The addition<sup>21</sup> of a large excess of *n*-pentane followed by filtration gave 54.1 mg, 62.2%, of black platelets.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{20}\text{F}_{12}\text{N}_2\text{S}_8\text{NiCu}$ : C, 24.82; H, 2.31. Found: C, 24.84; H, 2.43. The formation of this material as a salt was based on its conductance (1:1 electrolyte in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda_c = 67$  mhos), esr spectrum (a single line with no hyperfine structure,  $\langle g \rangle = 2.062$ ,  $\text{CH}_2\text{Cl}_2$  solution),<sup>22</sup> and cyclic voltammogram in  $\text{CH}_2\text{Cl}_2$  which was a superposition of those observed for reactants.<sup>23</sup>

**Visible Spectra.**—Visible and near-infrared spectra were recorded on Perkin-Elmer Model 450 and Cary Model 14 double-beam spectrophotometers. Low temperatures were maintained by placing the sample cell in a cooled brass holder which was enclosed by a dewar fitted with quartz windows.

**Infrared Spectra.**—Infrared spectra of KBr-disk samples were recorded on a Perkin-Elmer Model 621 grating spectrophotometer.

**Electrochemistry.**—Controlled-potential electrolysis and cyclic voltammetry was carried out using an instrument based on the design of Deford<sup>24</sup> and modified by Goolsby and Sawyer.<sup>25</sup> The measurements were made in acetone and dichloromethane using 0.1 *N* *n*-Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte. Potentials were measured at a gold electrode *vs.* a saturated calomel electrode fitted with a KCl-agar bridge which was separated from the solution by a fritted-glass disk. The concentrations of the solutions were 10<sup>-3</sup> *M*, and the temperature was 25°.

**Conductance Measurements.**—Molar conductances, at +25 and -78°, of 10<sup>-4</sup> *M* dichloromethane solutions were measured with an Industrial Instruments, Inc., Model RC-16B conductivity bridge using a cell equipped with platinum electrodes, calibrated with 0.1 *N* KCl. A 10<sup>-4</sup> *M* dichloromethane solution of the 1:1 salt (*n*-Bu<sub>4</sub>N)[Ni(tfd)<sub>2</sub>] was used for comparative purposes ( $\lambda_c = 66$  mhos).

**Electron Spin Resonance.**—The electron spin resonance spectra were obtained on a Varian Model V-4500 spectrophotometer using DPPH as an external standard.

**Temperature Measurement.**—Temperatures were measured using a Leeds and Northrup temperature potentiometer equipped with a copper-constantan thermocouple.

**Crystallography.**—Rhombohedral crystals of 4 were obtained by slow evaporation of a dichloromethane solution, and an equidimensional specimen 0.1 mm on an edge was selected for study. The unit cell constants  $a_0 = 7.793$  (3),  $b_0 = 12.880$  (7),  $c_0 = 9.624$  (6) Å and  $\alpha = 61.070$  (4),  $\beta = 111.380$  (2),  $\gamma = 108.030$  (4)° were determined from a least-squares fit of 12 carefully centered reflections using Mo  $K\alpha_1$  radiation ( $\lambda$  0.70926 Å). No symmetry was indicated by the preliminary precession and Weissenberg photographs, and since a Delaney reduction failed to reveal any hidden symmetry, the space group must be either *P*1 or  $\bar{P}$ 1. The assumption of one dimer per unit cell gave a density calculated from X-ray data of 1.86 g/cm<sup>3</sup> compared with 1.87 g/cm<sup>3</sup> obtained by flotation methods. Reflection data were collected under computer control using a Picker Model FACS II four-circle diffractometer with a crystal to scintillation detector distance of 32.0 cm and a pulse height analyzer adjusted to accept 90% of a reflection's intensity. The moving-crystal, moving-counter technique was used with a 2 $\theta$  scan rate of 1°/min and a scan range of (1.54 +  $\Delta$ ) where  $\Delta$  is included to account for the 2 $\theta$  separation of  $\alpha_1$  and  $\alpha_2$  peaks.

A total of 2275 reflections were measured in the limiting sphere having a maximum  $(\sin \theta)/\lambda$  of 0.54 Å<sup>-1</sup> using Mo  $K\alpha$  radiation made monochromatic by Bragg reflection from a graphite crystal. Background counts of 10 sec each were measured at the extremes of each 2 $\theta$  scan. Three standard reflections, remeasured every 50 reflections, showed only small statistical fluctua-

(18) Calculations by G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 3585 (1965), indicate that these bands represent optical transitions between the same molecular orbitals of the respective species and that the energy of the transition decreases with increased charge density on nickel dithiete.

(19) We have considered the possible combination of donor and acceptor levels for 1<sup>18</sup> and 2 [M. J. Week and J. P. Fackler, *Inorg. Chem.*, **7**, 2548 (1968)] and find that, even disregarding energetics, all reasonable acceptor orbitals of 2 are orthogonal to the donor orbitals of 1. Donation from 2 to 1, however, is allowed.

(20) G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier, Amsterdam, 1962.

(21) If allowed to stand, the solution decomposes, giving the mixed-ligand nickel dimer as one product; *vide supra*.

(22) Nickel dithiete monoanion has been reported to have an average  $g$  of 2.0618.<sup>6</sup>

(23) Copper bis(diethyldithiocarbamate) exhibits two electrochemically reversible processes, an oxidation at 0.46 V and a reduction at -0.50 V, both *vs.* sce in acetonitrile. Both the cation and anion show noticeable decomposition after 0.5 hr which is nearly complete in about 1 day. The oxidation wave is reported in ref 9 to be at 0.47 V in  $\text{CH}_2\text{Cl}_2$ .

(24) D. D. Deford, paper presented at the 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958.

(25) A. D. Goolsby and D. T. Sawyer, *Anal. Chem.*, **39**, 411 (1967).

tions during the data collection. Of the 2275 unique reflections measured, 1762 having intensities larger than  $3\sigma$  were considered to be observed. These were corrected for Lorentz and polarization effects but not for absorption, since the linear absorption coefficient was small ( $18.3 \text{ cm}^{-1}$ ). The range of transmission factors is 0.93–0.88.

An IBM 360-50 computer was used in all calculations,<sup>26</sup> and the function minimized in the least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ ,<sup>27</sup>

**Solution and Refinement of the Structure.**—A three-dimensional map of the Patterson function was interpreted to give the locations of five heavy atoms, which were assumed to be a nickel and four sulfur atoms. After improving their coordinates by two cycles of least-squares refinement, an electron density map was calculated which indicated the positions of the remaining nonhydrogen atoms. Nine further cycles of least-squares refinement of positional and isotropic thermal parameters gave  $R_1 = 0.116$  and  $R_2 = 0.165$ .<sup>28</sup>

(26) The programs used were local modifications of Eiss' REDAT for data reduction, Zalkin's FORDAP for Patterson and electron density maps, Busing, Levy, and Martin's ORFLS for least-squares refinement, Johnson's ORTEP for drawings, and Wood's MGEOM for distances, angles, and planes.

(27)  $w = 4F^2/L^2\sigma(I)$ , where  $L$  is the reciprocal Lorentz-polarization correction and  $\sigma(I) = [P + (t/20)^2B + (0.045I)^2]^{1/2}$ .  $P$  is the peak intensity,  $t$  the scan time in seconds, and  $B$  the total background count.

(28)  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$  and  $R_2 = (\sum w|F_o| - |F_c|)^2 / \sum wF_o^2$ <sup>1/2</sup>.

At this point all atoms except carbon and nitrogen were allowed to vibrate anisotropically, and the effect of anomalous scattering of the nickel atom was included in the refinement. Five additional cycles of least-squares refinement reduced  $R_1$  to 0.060 and  $R_2$  to 0.089.

An electron density difference map computed at this stage had its largest peaks in locations expected for most of the hydrogen atoms.

All atoms were now included in the refinement,<sup>29</sup> and four further cycles reduced  $R_1$  to 0.052.

The final weighted residue,  $R_2$ , is 0.071, and the standard deviation of an observation of unit weight, a rather large 2.4. The positional and thermal parameters are listed in Table I.<sup>30</sup> Tables II–V list derived parameters of interest.

(29) The atomic scattering power of Ni was corrected for the real and imaginary part of the anomalous dispersion: J. A. Ibers in "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202, Table 3.3.1A. Scattering powers for  $\text{Ni}^+$ ,  $\text{F}^-$ , and neutral S, N, C, and H were taken from D. H. Templeton, *ibid.*, p 202, Table 3.3.2B.

(30) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1415. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

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## The Crystal and Molecular Structure of Ammonium Pentachloronitrosylruthenate(II), $(\text{NH}_4)_2[\text{Ru}(\text{NO})\text{Cl}_5]$

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Received November 4, 1971

The crystal and molecular structure of ammonium pentachloronitrosylruthenate(II),  $(\text{NH}_4)_2[\text{Ru}(\text{NO})\text{Cl}_5]$ , has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in the space group  $D_4^2-P2_12_12_1$  of the orthorhombic system with four molecules in a cell of dimensions  $a = 10.534$  (3),  $b = 13.441$  (5), and  $c = 6.911$  (2) Å. The observed and calculated densities are 2.34 (2) and 2.337  $\text{g cm}^{-3}$ , respectively. Least-squares refinement of the structure has yielded a final value for the conventional  $R$  factor (on  $F$ ) of 0.022 for 1770 independent reflections having  $F^2 > 2\sigma(F^2)$ . The  $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$  anion is a slightly distorted octahedron with the Ru–Cl bond trans to the nitrosyl group shorter than the cis Ru–Cl bonds; the trans bond distance is 2.357 (1) Å while the cis bonds range from 2.373 (1) to 2.379 (2) Å. The Ru–N–O group is approximately linear, with an Ru–N–O bond angle of 176.7 (5)° and Ru–N and N–O bond distances of 1.738 (2) and 1.131 (3) Å, respectively. These values suggest that the nitrosyl group is bonded as  $\text{NO}^+$ . The observation that the Ru–Cl bond trans to the nitrosyl is shorter than those cis to the nitrosyl is in apparent contradiction to reported conclusions based on infrared spectroscopic data.

### Introduction

The nature of the bonding in transition metal–nitrosyl complexes has been the subject of much recent work,<sup>1–11</sup> and it has been concluded that the nitrosyl moiety bonds as  $\text{NO}^+$  to Ru(II) and other  $d^6$  systems.  $\text{NO}^+$  is an extremely efficient  $\pi$ -acceptor ligand<sup>12</sup> and,

like the isoelectronic CO and  $\text{CN}^-$  species, is a very strong trans-labilizing ligand in square-planar four-coordinate complexes.

Recently reported molecular orbital calculations for the complexes  $\text{Mn}(\text{CO})_5\text{X}$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ , have shown<sup>13</sup> that the Mn–X bond is entirely  $\sigma$  in nature and that the Mn–C bond trans to the halogen, while having much more  $\pi$  overlap, has slightly less  $\sigma$  overlap than the Mn–C bonds cis to the halogen—*i.e.*, that the halogen successfully competes with the carbonyl for  $\sigma$ -electron density. If it were also true that in complexes of the type  $\text{M}(\text{CO})\text{X}_5$  or  $\text{M}(\text{NO})\text{X}_5$  the M–X bonds are almost entirely  $\sigma$  in character and that the halogen competes successfully with the carbonyl or nitrosyl group for  $\sigma$ -electron density, then one would predict that the M–X bond trans to the carbonyl or nitrosyl would be stonger and shorter

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