Tabelle 7. *Vergleich von Wasserstoffbrückenabständen D(H)···A mit Ammonium-NH und mit Amido–NH als Donator*

	Ammonium-NH		Amido-NH	
Akzeptor	$NH_4[POS(NH_2)_2]$	$(NH_4)_2[PO_2S(NH_2)]$	$NH_4[POS(NH_2)_2]$	$(NH_4)_2[PO_2S(NH_2)]$
S	3,400 Å	3,312 Å 3,376	3,452 Å 3,484	3,478 Å
O	2,786 2,806	2,794 2,796 2,806 2,812 2,858	3,136	3,028
N	3,009	3,039	—	—

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The Structure of 2,2′-Dimercaptodiethylsulphidenickel(II). A Dimeric Molecule Containing Bridging Sulphur Atoms*

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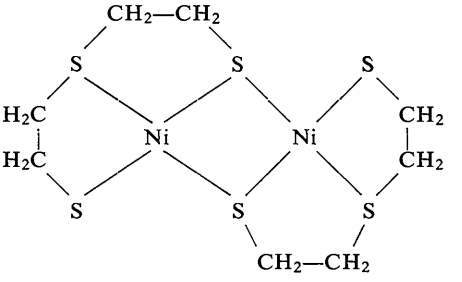
2,2′-Dimercaptodiethylsulphidenickel(II) crystallizes in the orthorhombic system, space group *Pbca*, with lattice constants $a=9{\cdot}46\pm0{\cdot}05$, $b=10{\cdot}93\pm0{\cdot}05$, and $c=28{\cdot}80\pm0{\cdot}15$ Å. The intensities of three-dimensional equi-inclination Weissenberg data were estimated visually and the structure was solved by Patterson and Fourier techniques. Refinement of atomic parameters was determined by the method of least squares. The molecules are dimeric with a formula unit $Ni_2S_6C_8H_{16}$. Each of the nickel atoms in the dimer is surrounded by four sulphur atoms in approximately square-planar arrangement, and one thiol sulphur of each ligand molecule is shared between a pair of nickel atoms forming two sulphur bridges. Ni–S bond lengths vary between 2·15–2·22 Å, the bridging bonds being longer than the terminal. The dimeric molecules are bent at the sulphur bridges and the dihedral angle between the mean planes of the sulphur atoms is 82° 18′. The bending of the molecule brings the two nickel atoms into unusually close proximity (2·73 Å) and the shape of the molecule is discussed in terms of metal–metal bonding and the steric requirements of the ligand.

Introduction

The compound 2,2′-dimercaptodiethylsulphidenickel(II) was first described by Harley-Mason (1952). Analysis showed that the complex contained one atom of nickel per molecule of dithiol and molecular weight determinations indicated that the formula unit was $Ni_2S_6C_8H_{16}$. From the red colour and solubility in organic solvents, Harley-Mason deduced that the complex was a non-ionic, square-planar complex of four-coordinate nickel, and proposed the bridged structure



The results of further work involving spectroscopic and magnetic studies (Barclay, McPartlin & Stephenson,

* A preliminary account of these results has been published (Barclay, Mc Partlin & Stephenson, 1967). A recent communication (Baker, Goodall & Moss, 1969) reports a second determination of this structure which entirely confirms our results.

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1968) are in agreement with the structure proposed by Harley-Mason.

2,2′-Dimercaptodiethylsulphidenickel(II) is remarkable in being an extremely soluble bridged complex in which the only donor atoms are sulphur atoms. Thiol ligands, in most cases, give polymeric complexes as a result of the formation of very stable bridges by the sulphur atoms. Further interest in the structure of this molecule lies in the configuration of the nickel and sulphur atoms; Harley-Mason considered them to be coplanar, but X-ray structure analyses of several thioloiron carbonyl complexes containing sulphur bridges (Dahl & Chin-Hsuan Wei, 1963, 1965) have shown the molecules to be sharply bent. Bis(ethylmercaptodinitrosyliron) $[C_5H_2SFe(NO)_2]_2$ has also been shown by X-ray analysis (Thomas, Robertson & Cox, 1958) to be a dimeric sulphur-bridged molecule with acute sulphur bridging angles which are possibly the result of metal–metal bonding within the molecule.

Experimental

Crystals of dimercaptodiethylsulphidenickel(II) were obtained by slow evaporation of a solution of the com-

Table 1. *Observed and calculated structure amplitudes for 2′2-dimercaptodiethylsulphidenickel* (II)

Scale: $\frac{1}{2}$ absolute.

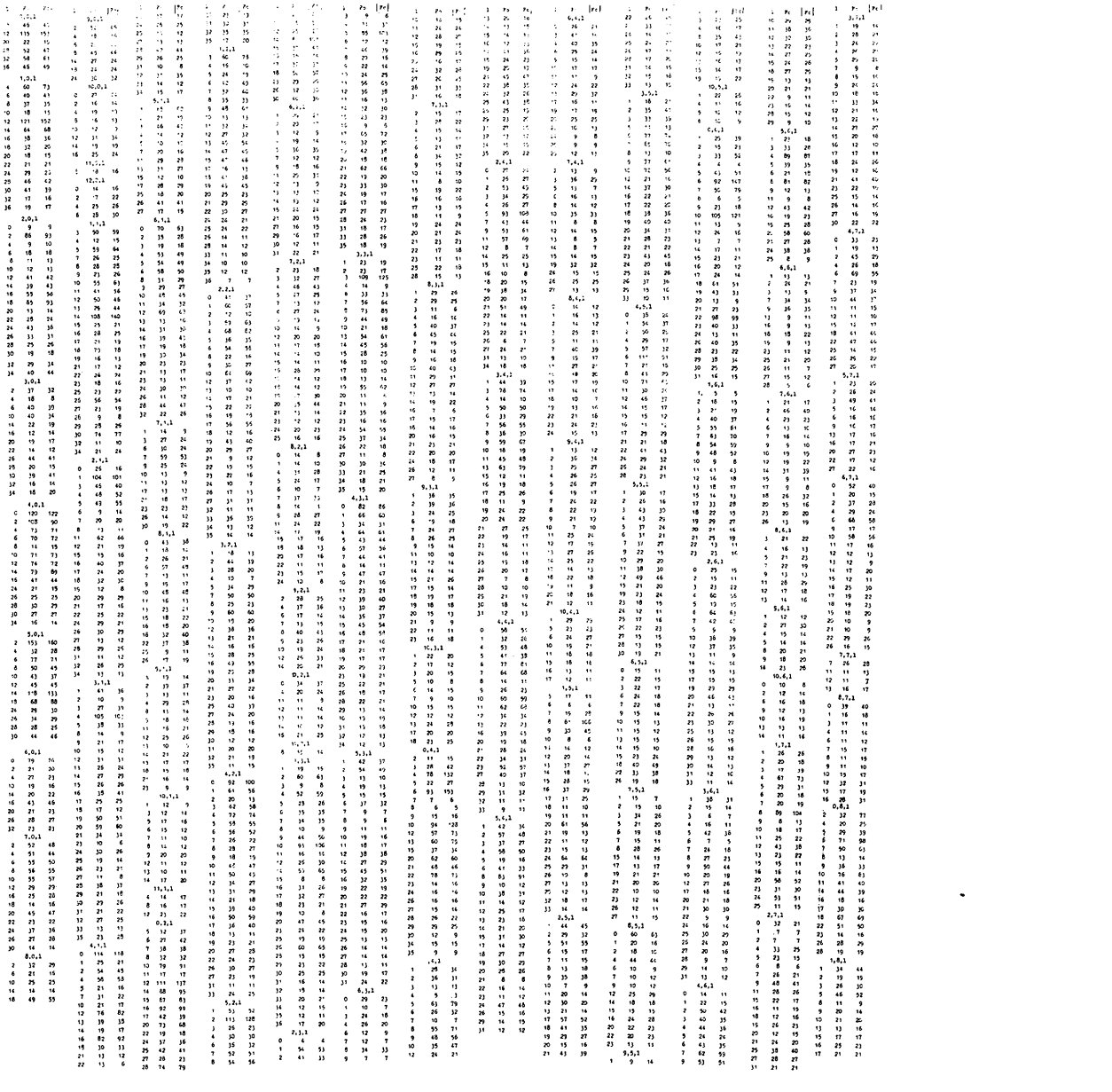


Table 1 (*cont.*)

	F_o	$\lvert F_c\rvert$
14	15	12
15	19	15
20	34	29
21	25	29
22	15	12
2,8,1		
0	41	37
2	16	13
3	22	21
4	12	11
5	15	11
6	15	12
8	15	13
9	15	14
11	19	15
13	25	27
16	30	28
17	11	12
18	26	27
19	13	13
20	11	6
21	15	14
22	20	21
23	10	12
25	16	13
26	9	8
27	18	17
28	17	15
29	15	15
3,8,1		
1	33	33
2	28	31
3	16	13
4	8	9
5	21	19
7	13	12
8	18	14
11	24	26
14	10	10
15	24	27
16	11	13
19	18	15
20	15	15
4,8,1		
0	41	33
1	23	19
2	19	11
3	46	40
5	17	14
6	36	26
7	28	24
10	10	10
13	21	23
14	21	16
16	26	30
18	26	22
19	23	22
21	17	18
22	26	26
26	12	11
5,8,1		
1	14	11
2	10	10
4	54	48
5	43	30
6	18	15
7	18	16
8	61	59
9	15	19
11	26	25
12	34	33
13	21	21
14	10	14
18	10	8
20	42	37
21	18	17
22	19	15
24	37	31
6,8,1		
0	15	10
1	18	14
2	21	20
3	11	9
7,8,1		
2	33	38
3	15	18
6	18	13
8	25	26
10	20	18
13	23	24
14	29	34
8,8,1		
0	24	18
1	27	25
3	19	17
16	8	7
19	4	4
20	13	9
1,9,1		
1	16	15
3	26	27
4	58	71
7	14	16
8	34	38
12	42	45
12	13	9
15	13	13
16	19	21
19	26	22
20	41	43
2,9,1		
1	42	37
2	29	24
3	25	15
5	22	21
6	21	19
7	11	12
8	19	21
10	21	20
3,9,1		
11	33	39
12	13	15
13	17	17
14	13	16
15	37	44
16	13	13
17	19	11
18	13	14
19	26	25
24	25	23
25	14	17
27	19	17
4,9,1		
1	23	25
2	46	43
3	19	15
4	27	21
7	17	17
8	21	18
9	25	21
10	22	19
11	26	26
12	13	10
13	26	30
14	24	29
15	25	27
17	23	20
18	13	18
19	12	8
23	17	18
24	17	19
25	22	21
26	14	18
27	18	22
4,9,1		
0	21	12
2	27	22
4	17	11
6	35	32
7	13	10
10	32	31
5,9,1		
3	26	18
5	19	14
7	26	24
8	37	45
9	23	22
6,9,1		
1	19	22
3	13	17
5	23	27
8	37	37
10	26	31
7,9,1		
1	22	24
3	18	17

plex in a mixture of chloroform and ethanol. Small, very dark red plates were formed. The unit-cell dimensions were obtained from zero-level precession photographs taken with Mo $K\alpha$ radiation.

2,2′-*Dimercaptodiethylsulphidenickel*(II)

$Ni_2S_6C_8H_{16}$, F.W. = 422.

Orthorhombic, $a = 9{\cdot}46 \pm 0{\cdot}05$, $b = 10{\cdot}93 \pm 0{\cdot}05$, $c = 28{\cdot}80 \pm 0{\cdot}15$ Å. $U = 2978$ Å^3, $Z = 8$, $D_m = 1.86$ g.cm^{-3} (by flotation), $D_c = 1{\cdot}88$ g.cm^{-3}, $F(000) = 1728$. Space group *Pbca* (D_{2h}^{15} No. 61), from systematic absences.

The intensity data were collected on multiple film equi-inclination Weissenberg photographs (Cu $K\alpha$) taken around [010], ($k = 0,1,---9$). Correlation data were obtained from zero level precession photographs and were adequate during the initial stages of the structure determination. Interlayer scale factors were introduced as variates during the final refinement stages.

Intensities were estimated visually with the aid of a calibration strip, and the Lorentz and polarization corrections were applied on UTECOM using the program of Rollett (1961). Neither extinction nor absorption corrections were applied to these data. The structure amplitudes were not scaled initially; the final scaling (Table 1) is based upon the calculated structure amplitudes.

Determination of the structure

Solution

The space group *Pbca* has eight general equivalent positions so that one molecule, $Ni_2S_6C_8H_{16}$, constitutes the asymmetric unit. Two factors complicated the interpretation of the three-dimensional Patterson function; the y coordinate of Ni(2) was very close to $b/4$ and the sum of the z coordinates of Ni(1) and Ni(2) was $C/4$. Thus, for example, the vector peak at $(0{\cdot}300, \frac{1}{2}, 0{\cdot}183)$ was at first interpreted as being the vector $(2x_1, \frac{1}{2}, \frac{1}{2} - 2z_1)$ but the correct interpretation proved to be $(2x_2, 2y_2, 2z_2)$. However, once this ambiguity was realized the positions of all atoms (except hydrogen) were obtained from the Patterson function and from successive difference-Fourier syntheses.

Refinement

The difference-Fourier syntheses mentioned above enabled corrections to be made to the positional parameters of atoms as they were located. Once all atoms had been positioned ($R = 0{\cdot}23$) the atomic parameters were refined by full-matrix least-squares methods in which the values of $\Sigma\, w(|F_o| - |F_c|)^2$ were minimized. Isotropic thermal parameters and interlayer scale factors were refined in addition to the positional parameters. Unit weights were used initially but this scheme was replaced after two cycles with one utilizing an estimated standard deviation in the observed structure amplitudes (F_o) of $F_o/10$. Unobserved data were not used in these least-squares calculations, which converged to give a final reliability index R of 0·14.

Two further refinement cycles in which only the anisotropic temperature parameters for each atom were allowed to vary, reduced the R index to 0·12. There is no justification in this procedure since the data were not rigidly internally scaled. However, the signs and magnitudes of the tensor components listed in Table 2 are reasonable and recent work by McConnell & Kastalsky (1969) and has shown that a thermal analysis based upon data collected and treated in the above manner can be meaningful. No attempt has been made in this present instance to analyse the thermal motions of the molecule.

Table 2. *Thermal exponent coefficients*

β_{ij} as given here are defined by:
$T = \exp[-10^{-4}(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + 2\beta_{13}hl + 2\beta_{13}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni(1)	73	38	4	7	3	−1
Ni(2)	69	31	5	−4	−1	1
S(1)	56	48	6	−7	−3	3
S(2)	89	29	6	23	−4	4
S(3)	82	90	5	14	1	−6
S(4)	72	42	6	−6	2	1
S(5)	90	31	6	1	−2	−4
S(6)	94	65	4	−2	−1	1
C(1)	80	56	8	−21	−1	−10
C(2)	91	51	7	13	−3	1
C(3)	121	108	7	31	3	−3
C(4)	113	50	8	43	4	5
C(5)	111	84	8	25	−6	−3
C(6)	69	33	8	0	−4	−4
C(7)	79	98	8	−5	4	12
C(8)	90	38	11	−16	2	2

For the calculation of structure factors the atomic scattering factors for Ni, S and C of Thomas & Umeda (1951), Dawson (1960) and Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used. A correction for the real component of the anomalous dispersion by Ni of Cu $K\alpha$ radiation was applied (Dauben & Templeton, 1955). UTECOM, an English electric DEUCE computer, was used for all calculations except the least-squares procedure, for which an IBM 7040 computer of the Australian Atomic Energy Commission was used. The programs used were those of Rollett (1961) and Busing, Martin & Levy (1962), respectively.

The final positional coordinates for the crystallographically independent atoms, together with average estimated standard deviations, are listed in Table 3. These coordinates together with unit-cell dimensions, were used to calculate the intra- and inter-molecular distances listed in Tables 4 and 5, and the bond angles listed in Table 6.

Table 3. *Atomic parameters for 2,2′-dimercaptodiethylsulphidenickel*(II)

Standard deviations are r.m.s. values based upon e.s.d.s along the three crystallographic directions.

	x/a	y/b	z/c	e.s.d. (Å)
Ni(1)	−0·04225	0·17715	0·15815	0·002
Ni(2)	0·15279	0·23529	0·09172	0·002
S(1)	−0·21065	0·05063	0·14333	0·004
S(2)	−0·07604	0·25958	0·08858	0·004
S(3)	0·17394	0·13745	0·02708	0·004
S(4)	0·37348	0·21339	0·10648	0·004
S(5)	0·12452	0·31489	0·16192	0·004
S(6)	0·01614	0·07841	0·22037	0·004
C(1)	−0·1586	0·0176	0·0836	0·016
C(2)	−0·1672	0·1305	0·0554	0·017
C(3)	0·3581	0·0906	0·0270	0·020
C(4)	0·4109	0·0734	0·0754	0·017
C(5)	0·3634	0·1591	0·1668	0·019
C(6)	0·2823	0·2639	0·1919	0·016
C(7)	−0·1147	−0·0433	0·2232	0·018
C(8)	−0·1616	−0·0820	0·1762	0·017

Table 4. *Selected interatomic distances* (Å) *in the molecule of 2′2-dimercaptodietthylsulphidenickel*(II)

The atomic numbering used is the same as in Table 3. Standard deviations are given in brackets and refer to the last one (or two) places of the preceding number.

Ni(1)–Ni(2)	2·733 (5)	S(6)–C(7)	1·819 (18)
–S(1)	2·152 (5)		
–S(2)	2·220 (5)	C(1)–C(2)	1·490 (24)
–S(5)	2·183 (5)	C(3)–C(4)	1·492 (26)
–S(6)	2·164 (5)	C(5)–C(6)	1·557 (25)
		C(7)–C(8)	1·485 (25)
Ni(2)–S(2)	2·183 (5)		
–S(3)	2·156 (5)		
–S(4)	2·144 (5)		
–S(5)	2·217 (5)		
S(1)—C(1)	1·825 (17)		
–C(8)	1·793 (17)		
S(2)—C(2)	1·909 (17)		
S(3)—C(3)	1·816 (20)		
S(4)—C(4)	1·808 (18)		
–C(5)	1·838 (19)		
S(5)—C(6)	1·813 (16)		

Table 5. *Intermolecular distances of less than* 4 Å *in the crystal of* 2,2′-*dimercaptodiethylsulphidenickel*(II)

The atomic numbering used is the same as in Table 3; the number in the second bracket denotes the following symmetry transformation:

	x	y	z
i	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\bar{z}$
ii	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iii	$\bar{x}$	$\bar{y}$	$\bar{z}$
iv	$\frac{1}{2}-x$	$\frac{1}{2}+y$	z
v	$\frac{1}{2}+x$	y	$\frac{1}{2}-z$
vi	$\bar{x}$	$\frac{1}{2}-y$	$\frac{1}{2}+z$

Ni(2)—C(4)(iv)	3·773
S(2)—C(4)(iv)	3·788
S(2)(i)—C(3)	3·761
S(3)—C(2)(i)	3·786
–C(2)(iii)	3·772
–C(1)(iii)	3·613
S(3)(iii)–C(2)	3·772
–C(1)	3·613
S(5)—C(4)(iv)	3·783
–C(5)(iv)	3·766
–C(7)(ii)	3·656
S(6)(v) –C(5)	3·665
–C(6)	3·922
C(1) —C(3)(iii)	3·887
C(2) —C(3)(iii)	3·839
C(2)(i) –C(3)	3·870
C(5) —C(7)(v)	3·871
C(6) —C(7)(iv)	3·890
–C(8)(iv)	2·989
–C(7)(ii)	3·597

Table 6. *Selected bond angles* (*degrees*) *in the* 2-2′ *dimercaptodiethylsulphidenickel* (II) *molecule*

The atomic numbering used is the same as in Table 3; standard deviations are given in brackets and refer to the last one (or two) places of the preceding number.

Ni(1)–S(2)—Ni(2)	76·7 (2)
Ni(1)–S(5)—Ni(2)	76·8 (2)
S(2)—Ni(1)–S(5)	82·5 (2)
S(2)—Ni(1)–S(1)	88·6 (2)

Table 6 (*cont.*)

S(1)—Ni(1)–S(6)	91·9 (2)
S(6)—Ni(1)–S(5)	96·8 (2)
S(2)—Ni(2)–S(5)	82·6 (2)
S(2)—Ni(2)–S(3)	96·7 (2)
S(3)—Ni(2)–S(4)	82·6 (2)
S(4)—Ni(2)–S(5)	88·9 (2)
Ni(1)–S(1)—C(1)	96·6 (6)
Ni(1)–S(1)—C(8)	102·9 (6)
C(8) –S(1)—C(1)	105·5 (8)
Ni(1)–S(2)—C(2)	102·5 (6)
Ni(2)–S(2)—C(2)	112·3 (6)
Ni(2)–S(3)—C(3)	103·3 (7)
Ni(2)–S(4)—C(4)	100·8 (6)
Ni(2)–S(4)—C(5)	100·0 (7)
C(4) –S(4)—C(5)	101·9 (9)
Ni(1)–S(5)—C(6)	114·0 (6)
Ni(2)–S(5)—C(6)	102·4 (6)
Ni(1)–S(6)—C(7)	103·2 (6)
S(1)—C(1) –C(2)	109·7 (12)
S(2)—C(6) –C(1)	108·5 (12)
S(3)—C(3) –C(4)	110·8 (14)
S(4)—C(4) –C(3)	106·9 (13)
S(4)—C(5) –C(6)	103·1 (12)
S(5)—C(6) –C(5)	114·2 (13)
S(6)—C(7) –C(8)	111·8 (13)
S(1)—C(8) –C(7)	109·2 (13)
S(1)—Ni(1)–S(5)	171·0 (2)
S(2)—Ni(1)–S(6)	170·7 (2)
S(2)—Ni(2)–S(4)	170·9 (2)
S(3)—Ni(2)–S(5)	173·3 (2)

Description of the structure

2,2′-Dimercaptodiethylsulphidenickel(II) has a dimeric molecule with the structure depicted in Fig. 1. Each of the nickel atoms in the dimer is surrounded by four sulphur atoms in approximately square-planar arrangement and one thiol sulphur of each ligand molecule is shared between a pair of nickel atoms forming two sulphur bridges. Distortions from the ideal square-planar configuration are evident in the S–Ni–S bond angles, the different lengths of the Ni–S bonds and the deviations of the atoms from the mean planes through the sulphur atoms. The equations of these planes, referred to the crystallographic axes, are given in Table 7 and indicate that there are significant distortions from planarity. The nickel atoms are each 0·1 Å above the mean plane of the sulphur atoms surrounding them.

The dimeric molecules are bent at the sulphur bridges and the dihedral angle between the mean planes of the sulphur atoms is 82° 18′. The bending of the molecule brings the two nickel atoms into unusually close proximity, the Ni(1)–Ni(2) distance being 2·73 Å, which is slightly greater than the interatomic distance of 2·50 Å found in nickel metal.

The agreement between equivalent bond lengths and angles in the two independent halves of the dimeric molecule is very good. The chemically equivalent bonds and angles involving only nickel and sulphur atoms occur in pairs of almost identical dimensions.

The nickel–sulphur bonds in the molecule are of three different chemical types. There are two tricovalent thioether sulphur atoms, each bonded to only one nickel atom; the lengths of these bonds, Ni(1)–S(1) and Ni(2)–S(4) are both 2·15 Å. Secondly, one of the thiol sulphur atoms in each ligand molecule is bicovalent and bonded to one nickel atom. These bonds, Ni(1)–S(6) and Ni(2)–S(3), have a length of 2·16 Å. These bonds are not significantly longer than the bonds from the two thioether sulphur atoms and both sets of bond lengths are close to values reported recently for other non-bridging Ni–S bonds in the bis(dithiomaleonitrile)nickelate(II) anion (2·16 Å, Eisenberg & Ibers, 1965), and in bisacetylbis(mercaptoethylimmine)-nickel(II), (2·16 Å, Fernando & Wheatley, 1965).

The third sulphur atom in each ligand molecule is a tricovalent bridging atom of a thiol group, and is bonded to both nickel atoms of the dimer. The first bond from each of these thiol sulphur atoms completes the second chelate ring of each monomeric unit. The lengths of these two bonds, Ni(1)–S(2) and Ni(2)–S(5), is 2·22 Å. The second bonds from these two thiol sulphurs are bridging bonds joining the two monomeric units to form the dimeric molecule. The length of the bonds, Ni(1)–S(5) and Ni(2)–S(2), is 2·18 Å. The chelate bond from each bridging thiol sulphur

Table 7. *Least-squares planes*

Equation in the form $Ax+By+Cz+D=O$, referred to the crystallographic axes, calculated after Schomaker, Waser, Marsh & Bergman (1959) with all weights equal to 1. All values have been multiplied by 10^3.

Plane	*A*	*B*	*C*	*D*	Atoms defining the plane			
I	−639	611	467	−3460	S(1)	S(2)	S(5)	S(6)
II	160	890	−426	−1297	S(2)	S(3)	S(4)	S(5)

Deviations from planes (10^{-3} Å)

Plane	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)	Ni(1)
I	79	−76	—	—	67	−70	105
II	—	25	−29	37	−33	—	—

Plane	Ni(2)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
I	—	−1260	−833	—	—	—	—
II	97	—	—	−204	−847	−1247	−658

Plane	C(7)	C(8)
I	−55	−661
II	—	—

atom, with a length of 2·22 Å, is significantly longer than any of the other nickel–sulphur bonds, and it is perhaps surprising that this bond is longer than the bonds which join the two halves of the molecule together. The lengths of the two sets of bonds from the bridging sulphur atoms (2·18 and 2·22 Å) are comparable with the length 2·20 Å reported (Woodward, Dahl, Abel & Crosse, 1965) for the Ni–S bonds from the bridging thiol sulphur atoms in the cyclic hexamer $[Ni(SC_2H_5)_2]_6$.

Carbon–sulphur bond distances, in the range 1·79–1·84 Å, do not differ significantly and the average value of 1·83 Å is similar to values reported in the literature, *e.g.* dimethyl sulphide, 1·82 Å; ethanedithiol, 1·81 Å. The carbon–carbon bond distances in the molecule all lie in the range 1·49–1·56 Å and, as the estimated stan-

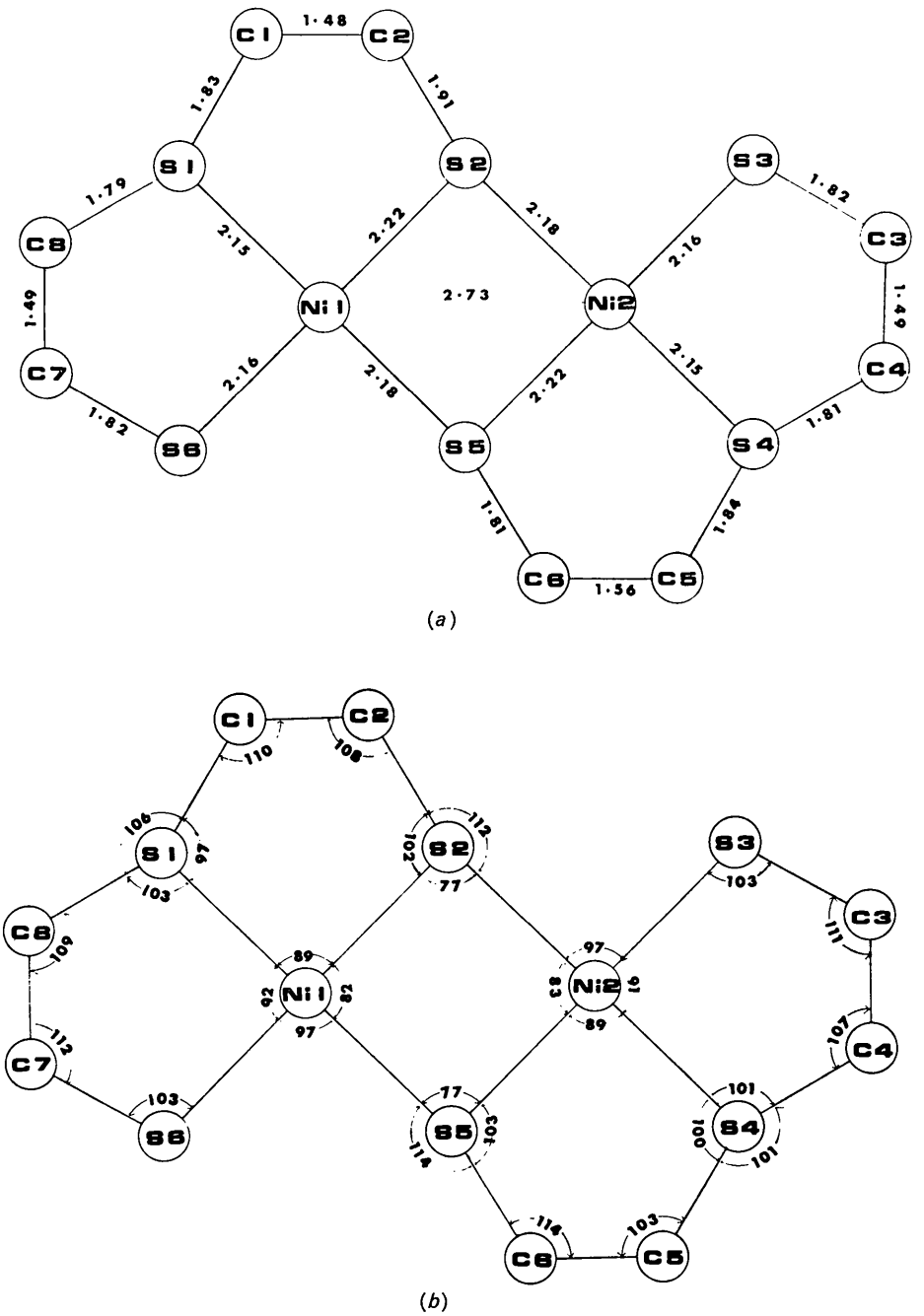


Fig. 1. A depiction of the molecule of 2,2′-dimercaptodiethylsulphidenickel(II) showing (*a*) bond distances and (*b*) angles.

dard deviations for these bonds is 0·03 Å, there appear to be no significant differences in their lengths. The mean distance of 1·51 Å is not significantly different from the value of 1·54 Å, which is the mean of the values listed by Ham (1961) for single bonds between sp^3 hybridized carbon atoms.

The Ni–S–Ni angles of 77° are unusually small for tricovalent sulphur atoms. The angles of 83° in the hexamer $[Ni(SC_2H_5)_2]_6$, however, also show considerable distortion; even smaller angles are reported in the molecules $[C_2H_5SFe(NO)_2]_2$, 73·7° (Thomas, Robertson & Cox, 1958), and $[C_2H_5SFe(CO)_3]_2$, 68·3° (Dahl & Chin-Hsuan Wei, 1963.

The sulphur atoms S(6) and S(3) are two-covalent, and the C–S–Ni bond angles (103°) are similar to those reported for other two-covalent sulphur atoms, *viz.* 105° in dimethyl sulphide (Allen & Sutton, 1950), 104° in dimethyl sulphide (Stevenson & Beach, 1938), and 98° in 2,2′-diiododiethyl trisulphide (Donohue, 1950.)

The three-covalent sulphur atoms S(1) and S(4) would be expected to have a pyramidal configuration and the observed bond angles, in the range 97°–106°, are approximately those to be expected for this stereochemical arrangement.

The remaining two sulphur atoms S(2) and S(5) are the bridging atoms and are each joined to two nickel atoms and a carbon atom. Both these sulphur atoms have pyramidal configuration, but the bond angles are grossly distorted from their expected values. However, the values in the two halves of the dimer are consistent, with mean values for <Ni–S–Ni, of 77°; <Ni–S–C, 103°; and <C–S–Ni, 113°.

The distortion in the bond angles around the bridging sulphur atoms apparently results from the stereochemical requirements of the ligand in the formation of the dimer, the observed values being those which impose the least steric strain in the molecule as a whole. Models indicate that in a less bent molecular structure the Ni–S–C bond would be larger still, and in the extreme case of a flat molecule, the value would be close to 180°. A less bent molecule would allow the Ni–S–Ni angle to increase to a more normal value. On the other hand, more acute bending of the molecule would reduce the Ni–S–C angle to a value closer to the ideal tetrahedral value, but there would be simultaneous reduction in the size of the Ni–S–Ni angle to a value even lower than 77°.

The orientation of the carbon atoms in the $-CH_2-CH_2-$ bridges is of particular interest. It was mentioned in the introduction that Harley-Mason predicted that the nickel and sulphur atoms would be coplanar, in which case the possibility of isomerism exists owing to differing orientations of the carbon bridges with respect to this plane. The pyramidal configuration of the three-covalent thioether sulphur atom would mean that the chelate rings are bent with the $-CH_2-CH_2-$ groups in one half of the molecule either both above or both below the molecular plane. Two molecular forms thus arise – a *cis* isomer with all four $-CH_2-CH_2$ groups of the molecule bent to the same side of the molecular plane, or a *trans* isomer with the $-CH_2-CH_2-$ groups of one half of the molecule above the plane, and those of the other half below the plane.

The present structure analysis shows that the carbon atoms in both halves of the molecule are *below* the mean planes of the sulphur atoms, that is, the chelate rings are bent in the same direction as the molecule as a whole. The nickel atoms, as mentioned earlier, are slightly *above* these planes. In the bent molecule the two possible orientations for the $-CH_2-CH_2-$ groups, above and below the planes of the sulphur atoms, are no longer equivalent. Therefore, the possibility of three isomeric forms exists. As well as the *trans* isomer with $-CH_2-CH_2-$ groups in opposite halves of the molecule above and below the planes of the sulphur atoms, there are two possible *cis* isomers in which the $-CH_2-CH_2-$ groups are either all above the planes or all below the planes. As the two configurations for the $-CH_2-CH_2-$ groups above and below the planes of the sulphur atoms are not equivalent, it would be expected that all four groups in the dimer would adopt whichever of these configurations involved least steric strain. This suggests that a *cis* isomer is a more probable structure than a *trans* isomer and the structure analysis results do indeed show that all the carbon atoms are below the mean planes of the sulphur atoms, giving rise to a *cis* isomer. The deviations of the carbon atoms from these planes are given in Table 7.

It might be expected that there would be good agreement between the distances of chemically equivalent carbon atoms from their respective least-squares planes. This would give a symmetrical molecule with the two halves approximately related by a twofold axis through the midpoint of the line joining the two nickel atoms and the two bridging sulphur atoms. However, the only pair of equivalent carbon atoms which are the same distance below the sulphur planes are C(1) and C(5), which are 1·26 Å and 1·25 Å, respectively below the sulphur planes. Each of the other chemically equivalent pairs of carbon atoms show a discrepancy of nearly 0·2 Å in their distances from the mean planes through the sulphur atoms. These differences are most likely to be a result of differences in environment brought about by the manner in which the molecules are packed in the crystal. The equivalent atoms C(7) and C(3), for example, are 0·05 Å and 0·20 Å, respectively below the planes of the sulphur atoms. This difference may be explained by the fact that C(7) is only 3·60 Å away from C(6) of an adjacent molecule and any further deviation of C(7) from the plane of the sulphur atoms would bring it even closer to this atom. The chemically equivalent atom C(3), which is much further below the plane, has no neighbouring atom nearer than 3·8 Å.

The molecules are arranged obliquely in rows parallel to [100] and the (100) and (010) projections, shown in Fig. 2, illustrate the packing arrangements of the

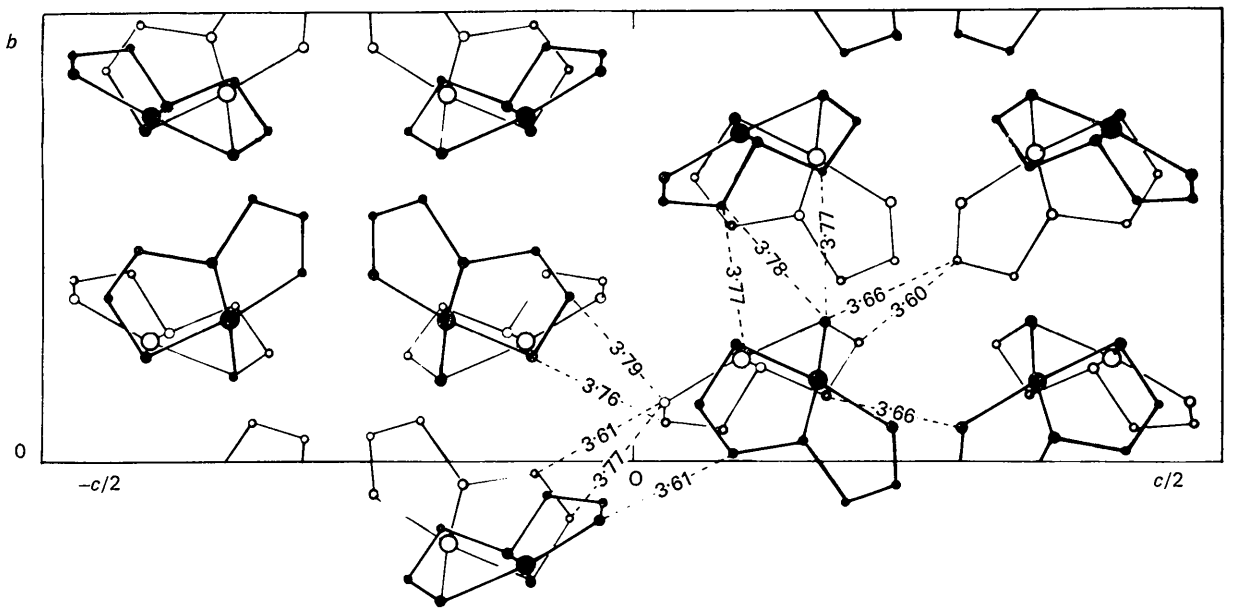
dimeric molecules. Adjacent rows of molecules are related by glide planes. The interatomic distances between molecules are listed in Table 5.

There is no evidence of intermolecular interaction along the approximately tetragonal axes of the nickel atoms. Closest approaches to the metal atoms are C(4) (iii) which is 3·77 Å from Ni(2) and C(7) (ii), which is 4·82 Å from Ni(1). The distance between the nickel atoms of one molecule and the molecule lying immediately above is 10·93 Å. The closest intermolecular approach is 3·60 Å between C(6) and C(7) (vi), which is of the order expected for van der Waals approach distances.

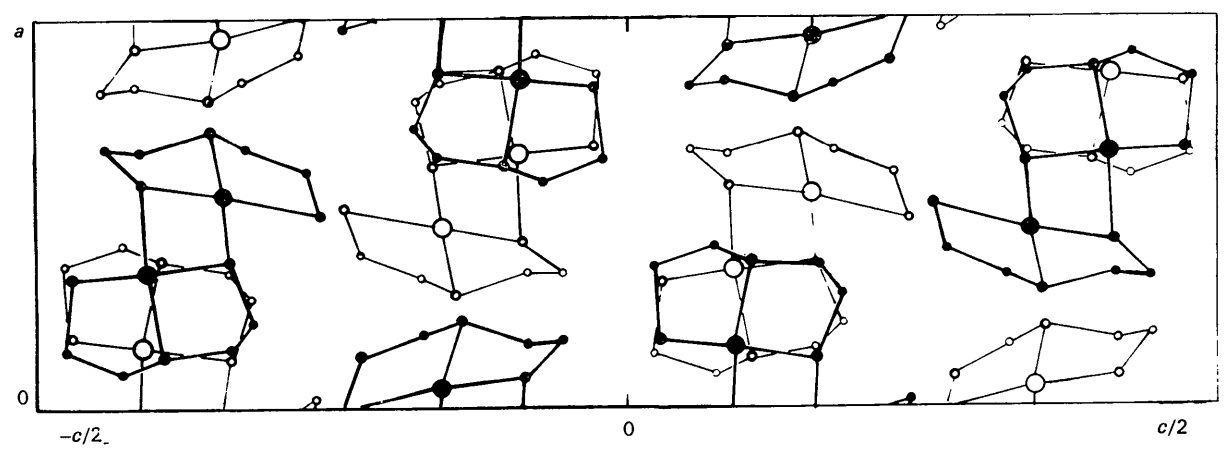
Metal–metal bonds

Metal–metal interaction has been postulated for every element in the transition block except the scandium triad (Lewis, 1965).

Many of the complexes in which metal–metal interaction occurs are binuclear bridged molecules with short distances between the metal atoms. The present



(a)



(b)

Fig. 2. Projection of the structure of 2,2′-dimercaptodiethylsulphidenickel(II) onto the (*a*) (100) and (*b*) (010) planes. Some close intermolecular approach distances are shown.

work has shown that 2,2′-dimercaptodiethylsulphidenickel(II) is a dinuclear complex in which the molecule is bent about the bridging sulphur atoms in such a way that the nickel atoms are in unusually close proximity. It is, therefore, of interest to discuss the methods that have been used to detect metal–metal bonding in other complexes.

One of the most common methods of detecting metal–metal interaction is the determination of magnetic properties. Unexpected diamagnetism or markedly reduced paramagnetism in complexes are taken as an indication of metal–metal bonding. An example of this is given by the two chloro-bridged, dimeric molybdenum complexes $[MoCl_5]_2$ and $[Mo(OC_6H_5)_3Cl_2]_2$. Molybdenum pentachloride has a temperature dependent paramagnetism which is $1{\cdot}65\beta$ at room temperature (Klem & Steinberg, 1936) and is close to the value found for other molybdenum(V) complexes. For example, the sodium salt of the ion MoF_6 has a moment of $1{\cdot}66\beta$. The phenoxide complex, however, is virtually diamagnetic (Mitchell & Williams, 1962). This is attributed to spin-pairing in a metal–metal bond in the latter compound.

The ultraviolet and visible spectroscopic properties of metal–metal systems have not been extensively investigated. However, for the dinuclear copper(II) complexes of aliphatic carboxylic acids, an absorption band at 375 mμ has been associated with molecules showing Cu–Cu interaction (Forster & Ballhausen, 1962). The polarized spectra of some complexes have been used to suggest metal–metal bonds (Yamada, 1953).

The existence of metal–metal bonds in many cases has been confirmed by X-ray structure determination. It is difficult to select criteria for distances between metal atoms consistent with metal–metal bonding. Reference is often made to the interatomic distance in the pure metal. Metal atoms in a compound which are as close or closer than they would be in the metal are considered to be bonded to each other. There are, however, many examples of metal–metal bonds in which the separation of the metal atoms is greater than the interatomic distance in the metal. The π-cyclopentadienyl tricarbonyl molybdenum molecule, for example, has been shown by X-ray structure determination to be a dimer in which the two halves are linked only by a metal–metal bond. The molecular structure is shown in Fig. 3(*a*). However, the Mo–Mo distance of 3·22 Å is considerably longer than the interatomic distance in the metal of 2·73 Å (Wilson & Schoemaker, 1957).

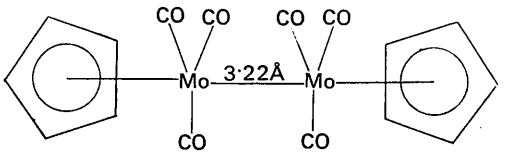
X-ray determination of the structure of the magnetically normal molybdenum pentachloride has shown that the Mo–Mo distance is 3·84 Å (Sands & Zalkin, 1959). The metal–metal bond in the analogous compound, $[Mo(OC_6H_5)_3Cl_2]$, indicated by the extremely low magnetic moment, is confirmed by the very much shorter Mo–Mo distance of 2·8 Å. This is close to the interatomic distance of 2·73 Å observed in the metal (Mitchell & Williams, 1962).

The rhenium(III) chloride anion is an example of a compound where magnetic evidence did not indicate a metal–metal bond. The diamagnetic character was explained in terms of a tetrahedral ion $ReCl_4^-$ in which the four *d*-electrons are paired in the lower d_γ orbitals (Orgel, 1956). X-ray structure determination, however, has shown that it is, in fact, a trinuclear anion, $Re_3Cl_{12}^{3-}$, in which the rhenium atoms are bonded to each other, lying at 2·47 Å apart at the corners of an equilateral triangle as shown in Fig. 3(*b*) (Robinson, Ferguson & Penfold, 1963; Bertrand, Cotton & Dollase, 1963).

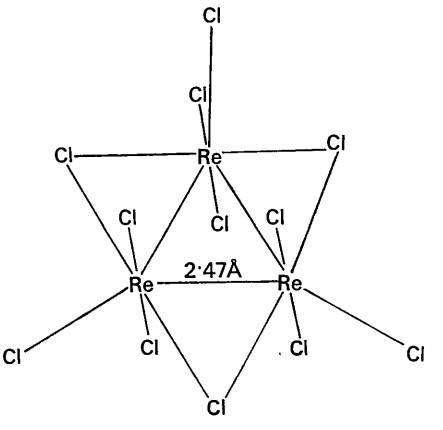
In the present work the X-ray determination of the structure of dimercaptodiethylsulphidenickel(II) shows that the molecule has a Ni–Ni distance of 2·73 Å which is greater than the interatomic distance of 2·50 Å in nickel metal. It is sufficiently close, however, for possible metal–metal interaction. Nickel(II) in square planar configuration is already spin-paired, which rules out the possibility of detecting such interaction by magnetic measurements.

It is of interest to make a structural comparison of dimercaptodiethylsulphidenickel(II) with other sulphur-bridged molecules in which metal–metal bonding has been confirmed by magnetic measurements and X-ray structure analysis.

Many metal carbonyl and π-cyclopentadienyl compounds are known in which two metals are bridged by sulphur atoms, and they are all diamagnetic (Stone,



(*a*)



(*b*)

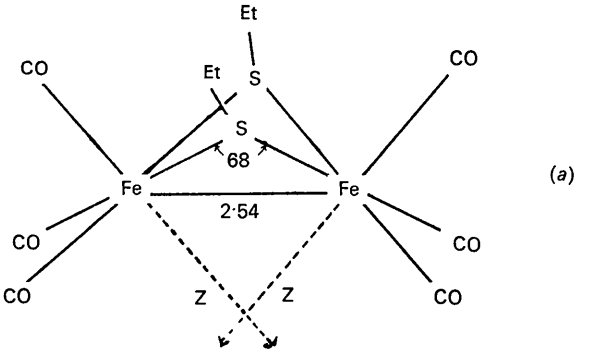
Fig. 3. (*a*) The π-cyclopentadienyl tricarbonyl molybdenum dimeric molecule showing metal–metal bonding. (*b*) The trinuclear anion $Re_3Cl_{12}^{3-}$ in which Re–Re bonding occurs.

1965). To explain this fact, electron pairing in metal–metal bonds was postulated for these compounds.

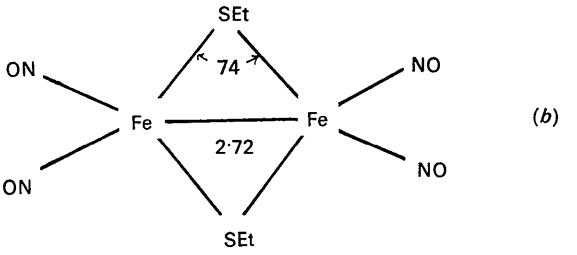
Dahl & Chin-Hsuan Wei (1963), determined the structure of one of these diamagnetic compounds, $[C_2H_5SFe(CO)_3]_2$, and showed that the molecular geometry was consistent with a bent metal–metal bond [Fig. 4(*a*)]. The Fe distance is 2·54 Å which is very close to that of 2·52 Å found in the metal. Each iron atom is surrounded by three carbonyl groups and two sulphur atoms at the corners of a distorted tetragonal pyramid. The tetragonal axes of the two iron atoms meet at an angle of 113°, allowing considerable overlap of the octahedral orbitals. Dahl & Chin-Hsuan Wei suggested that the sharp Fe–S–Fe bridge angles of 68·3° are due primarily to the energy gained from better overlap of the two iron orbitals with each other, forming a bent metal–metal bond.

The compound, $[C_2H_5SFe(NO)_2]_2$, also has a sulphur-bridged dimeric molecule with a metal–metal bond. This was indicated by the fact that it was also diamagnetic (Cambi & Szego, 1931) and was confirmed by X-ray structure determination (Thomas, Robertson & Cox, 1958). The molecular structure is shown in Fig. 4(*b*). It has a Fe–S–Fe bridging angle of 73·7° and metal–metal distance of 2·72 Å, which is rather longer than that of 2·52 Å found in the metal.

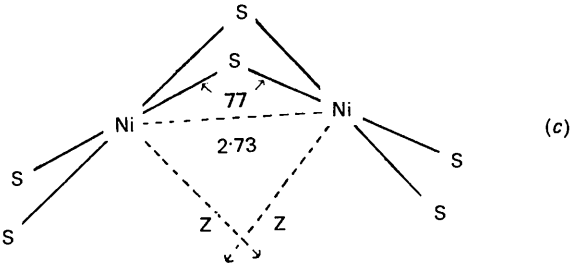
The geometry of these two sulphur-bridged compounds has certain similarities to that of dimercaptodiethylsulphidenickel(II) which is shown for comparison in Fig. 4(*c*). The iron carbonyl and the nickel complexes both have dimeric molecules sharply bent about



The structure of the molecule $[C_2H_5SFe(CO)_3]_2$



The structure of the molecule $[C_2H_5SFe(NO)_2]_2$



The environment of the nickel in 2,2′- dimercaptodiethylsulphidenickel (II)

Fig. 4. Molecules in which 'bent' metal–metal bonding may occur.

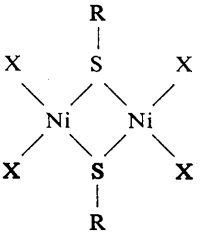
the sulphur bridge, and the nitrosyl compound has a planar arrangement of the Fe–S–Fe–S group with a very similar Fe–S–Fe angle. The Ni–S–Ni bridging angle of 77° is not as acute as those of the two iron complexes (68·3° and 74°), but still remarkably small and very much less than the approximately tetrahedral angle expected for a sulphur atom using sp^3 hybrid orbitals. The Ni–Ni distance is 2·73 Å, which is greater than the interatomic distance of 2·50 Å found in nickel metal. However, the Fe–Fe distance in the nitrosyl compound and the corresponding interatomic distance in iron metal are very similar in relative magnitude, being 2·72 Å and 2·52 Å, respectively.

As previously mentioned, the square-planar nickel complex, unlike the other two compounds, would be diamagnetic whether or not metal–metal interaction occurred. In particular, the octahedral orbitals in the nickel complex both contain a pair of electrons. This might appear to preclude the idea of any bent metal–metal bond of the type found in the iron carbonyl complex. Nickel–nickel bonds along the tetragonal axes have, however, been postulated for the diamagnetic square-planar complex, bis(dimethylglyoximato)nickel(II). Godycki & Rundle (1953) showed, in an X-ray structure determination, that the planar molecules are packed in layers with the nickel atoms lying vertically above each other at a distance of 3·25 Å apart. To account for the extreme insolubility of the complex, they postulated that one of the non-bonding electrons in the $3d_{z^2}$ orbital of each nickel atom is promoted to the vacant $4p$ orbital and that subsequent overlap of half-filled orbitals in adjacent metal atoms bonded the molecules together. The configuration of the metal would, therefore, be octahedral using d^2sp^3 hybrid orbitals. Later, Rundle (1957) published a molecular orbital treatment of these bonds. Yamada (1953) found that the polarized spectra of the bis(dimethylglyoximato) complexes of nickel(II), palladium(II), platinum(II) and gold(III) were consistent with metal–metal interaction along the tetragonal axes.

The possibility exists, therefore, that there is a metal–metal interaction in dimercaptodiethylsulphidenickel(II), using the vacant $4p$ orbitals and the full $3d_{z^2}$ orbital of both nickel atoms.

The question remains as to whether such a metal–metal interaction could be responsible for the very sharp bending of the nickel dimer at the sulphur bridges, or whether the steric requirements of the sulphur atoms are alone responsible for the geometry of the molecule, and any metal–metal interaction is a secondary effect as a result of the accidental proximity of the two nickel atoms. The situation may be similar to that which exists in the trimeric molecule of bis(acetylacetonato)nickel(II) where octahedral configuration is achieved by adjacent octahedra sharing three oxygen atoms. This means that the three nickel atoms are held at a distance of 2·90 Å apart by geometric factors alone (Bullen, Mason & Pauling, 1965). There is no magnetic evidence of metal–metal bonding in this case, as the moment is 3·20β, which is normal for spin-free nickel(II) complexes with octahedral configuration (Cambi & Szego, 1931).

The X-ray structure determination of a square-planar nickel complex bridged by a monodentate sulphur ligand would throw some light on whether metal–metal interaction is a primary factor in determining the geometry of sulphur-bridged nickel complexes. If a molecule of the type



was found to be bent about the sulphur-bridge, then this could reasonably be attributed to metal–metal interaction, as in this case the sulphur atoms would most nearly obtain a tetrahedral configuration in a planar molecule, with the organic group, R, above or below the plane.

Interaction between the nickel atoms in dimercaptodiethylsulphidenickel(II) might account for the fact that it, alone out of all the complexes prepared, was a soluble dimer.

Molecular models suggest that the dimeric structure involves considerably more steric strain than the trimeric dimercaptodiethylsulphidepalladium (Barclay *et. al.*, 1967). The bond angles at the sulphur atom also suggest that there is less strain in the trimeric molecule. It may, therefore, be interaction between the metal atoms in dimercaptodiethylsulphidenickel that makes it form dimeric molecules instead of some sterically less strained molecule such as that of the palladium complex. The tendency for metal–metal bond formation usually increases for second and third row transition metals, so that normally, palladium would be expected to form metal–metal bonds more readily than nickel. However, if a bent bond, similar to that postulated by Dahl *et al.* (1963) for the iron compounds is formed, the relative tendency to interact would depend on the ease with which the third np and the $(n-1)d_{z^2}$ orbitals can be hybridized with the $(n-1)dnsnp^2$ orbitals (Nyholm, 1961). It is well established that nickel forms five and six-coordinate complexes more readily than palladium and platinum, so that one would expect metal–metal interaction of this type to be greater for nickel than for the other metals.

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The Influence of Valence Electron Scattering on the Results of X-ray Structure Analyses

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The influence of valence electron scattering on the results derived from the least-squares refinement of single-crystal X-ray diffraction data has been examined for the structure of taurine, 2-aminoethylsulphonic acid. The parameters derived from a refinement including only high order reflexions ($\sin\theta/\lambda >$ 0·65 Å^{-1}), which are relatively unaffected by valence electron scattering, are compared with those from a low order ($\sin\theta/\lambda < 0{\cdot}65$ Å^{-1}) refinement. An analysis of the difference Fourier syntheses indicates that features attributable to the valence electrons are systematically modified in the low-order treatment.

Introduction

Current X-ray refinement techniques are based on spherically averaged form-factor curves and thus the redistribution of valence electrons in bonded atoms is ignored. In the least-squares procedure, aspherical scattering effects can be absorbed by both the anisotropic temperature factors and by movement of the atomic centre. This may lead to significant errors in the structural parameters and may also result in the loss of important information about the valence electron distribution.

Dawson (1964) has examined a hypothetical structure consisting of two sp^3 'prepared' state nitrogen atoms and found that least-squares positional parameters are in error by about 0·02 Å when conventional atomic scattering factors are used. O'Connell, Rae & Maslen (1966) have extended Cochran's (1956) calculations of the electron distribution in benzene. They have shown that the asymmetric environment of the