The Crystal Structure of Bis-(*cis*-1,2-diphenylethene-1,2-dithiolato)nickel

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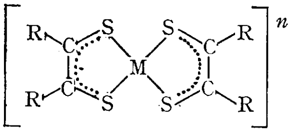
SINCE their discovery by Schrauzer and Mayweg[1] compounds of general formula (I) have been subjected to intensive investigation.[2]



(I)

They are remarkable in that *n* may have values of 0, -1, and -2 for the same metal M and substituents R. There is doubt about the oxidation state of the metal in the compounds with $n = 0$ and -1 and consequently about the naming of the complexes. We have followed the non-committal name suggested by Eisenberg and Ibers[3] for the rhenium compound.

We report the crystal structure analysis of the complex with M = Ni, R = Ph and $n = 0$, the first to be prepared by Schrauzer and Mayweg who gave us the black crystals. In a monoclinic unit cell having $a = 5{\cdot}835$, $b = 10{\cdot}970$, and $c = 18{\cdot}35$ Å, $\beta = 91{\cdot}4°$ and space group $P2_1/a$, there are two molecules, so the nickel atom occupies a centre of symmetry. Three dimensional observations were

TABLE. *Bond lengths in chelate rings,* Å.

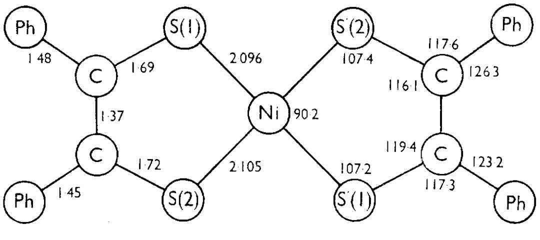
	$n = 0$	$n = 0$	$n = -1$	$n = -2$
	M = Co, R = CF_3[6]	M = Ni, R = Ph	M = Ni, R = CN[7]	M = Ni, R = CN[8]
M–S	2·16 ± 0·016	2·101 ± 0·002	2·146 ± 0·001	2·165 ± 0·005
C–S	$1{\cdot}69_4$ ± 0·016	1·71 ± 0·01	1·714 ± 0·004	1·75 ± 0·01
C–C	1·39 ± 0·02	1·37 ± 0·014	1·356 ± 0·007	1·33 ± 0·02

made photographically on a crystal cooled to 100°K, to give 1653 independent structure amplitudes.

The sulphur atoms were located from a three-dimensional Patterson synthesis, the carbon atoms from successive Fourier difference syntheses. Hydrogen atoms were deduced from geometrical considerations. Anisotropic refinement for the heavier atoms and isotropic refinement for the hydrogen atoms were carried out by least-squares until *R* was 0·11.

In phenyl groups the average C–C bond length is 1·38 Å; the standard deviation, calculated from the agreement between the 12 values, is 0·01 Å; this indicates that the standard deviations given by the least-squares programme, 0·014 Å in a C–C bond, are a satisfactory indication of precision. Each phenyl group is planar and neither is conjugated with the chelate ring, the dihedral angles being, 66° and 33°.

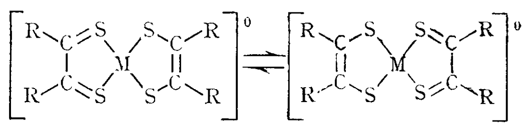
In the Figure the bond lengths and angles in the chelate ring are shown. The environment of the nickel is strictly square planar, the nearest other neighbours are a sulphur atom at 4·6 Å, two hydrogen atoms at 3·2 Å and two phenyl carbon atoms at 4·1 Å.



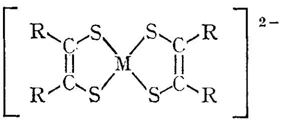
FIGURE

Bond lengths, Å, *and angles in the chelate ring. The standard deviations in the bond lengths are* 0·002 Å *in Ni–S,* 0·01 Å *in C–S, and* 0·014 Å *in C–C. The standard deviations in the angles are* 0·1°, 0·3°, and 0·8° *round Ni, S, and C respectively.*

Comparable bond lengths from structure determinations with standard deviations in C–C of 0·02 Å, or better, are collected in the Table. It can be seen that the trend of the differences in the bond lengths confirms the theory of Schrauzer and Mayweg,[4,5] that the variations in *n* do not correspond to changes of oxidation state of the metal but result from extensive ground-state delocalization, or, in the valence bond representation:



while the anion with $n = -2$ is:



A possible complication is that in the compound[6] with M = Co, R = CF_3, $n = 0$ the metal is actually five-co-ordinated with a fifth Co–S bond of 2·38 Å; and a weak Ni–S interaction at 3·59 Å was considered as an explanation of the magnetic moment of the compound[7] M = Ni, R = CN, $n = -1$. The compound with M = Ni, R = CN, and $n = -2$ is four-co-ordinated and strictly comparable with ours.

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