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Electron diffraction by the vapor of Ni(CO)₄ leads to a molecular model in which the four carbonyl groups have a tetrahedral arrangement about the nickel atom with the distances $Ni-C = 1.82 \pm 0.03A$ and $C-O = 1.15A$. These distances are compatible with resonance between two electronic structures in which the $C-O$ bond resonates between triple and double electron pair bonds and the

Ni$-$C bond between single and double electron pair bonds. Nickel carbonyl is the first quadricovalent compound of neutral nickel whose structure has been determined, and its tetrahedral configuration is contrasted with the square arrangement of bonds in the quadricovalent compounds of divalent nickel ion.

THE molecular structure of nickel carbonyl and its relation to the more general problem of the orientation of the four bonds in quadricovalent nickel compounds has interested chemists for more than ten years. In 1926 Blanchard and Gilliland[1] gave a detailed discussion of the chemical properties of nickel carbonyl and deduced an electronic structure which was intended to be compatible with these properties and at the same time would allow for a complete shell of eighteen electrons around the nickel atom. It is interesting to note that their suggestion that four electrons are shared between each carbon and the nickel atom is equivalent in the modern concept of valence to double electron pair bonds between the carbon and nickel atoms, to which we shall resort in order to account for our observations.

In 1930 Sugden[2] proposed a cyclic structure for nickel carbonyl in which the nickel and the four carbon atoms form a five-membered ring with an oxygen atom attached to each carbon.

Pauling[3] predicted from a theoretical consideration of the relative strengths of bonds formed by s, p, and d eigenfunctions that in the compounds of divalent nickel ion in which four covalent bonds are attached to the nickel atom the four bonds should be directed toward the corners of a square. In support of this prediction he cited the isomorphism of $K_2Ni(CN)_4 \cdot H_2O$

with the corresponding palladium compound and the known[4] square arrangement of the bonds in the chloropalladites and chloroplatinites. Because of later misinterpretations it should be pointed out that the same theoretical considerations suggest a tetrahedral arrangement when four bonds are formed with neutral nickel, as in the case of nickel carbonyl.

Sugden[5] found further evidence in favor of the square arrangement in quadricovalent nickelous compounds in the preparation of interconvertible isomers of the nickel derivatives of methyl benzyl-, methyl n-propyl-, and methyl n-butyl glyoxime. These were explained as cis- and trans-isomers, which could not exist with a tetrahedral arrangement of the four bonds. A similar relation was found much earlier by Tschugaeff[6] for the nickel derivatives of monoethylglyoxime but he made no attempt to explain this isomerism. Additional crystallographic evidence is found in the isomorphism[7] of $BaNi(CN)_4 \cdot 4H_2O$ and $BaPt(CN)_4 \cdot 4H_2O$. Even more conclusive is the recent work of Cox, Pinkard, Wardlaw and Webster[8] on the nickelous derivative of salicylaldoxime in which two molecules of the aldoxime are joined by four bonds to the nickel atom. Oscillation and rotation x-ray photographs show that the crystal belongs to the space group $P2_1/m - C_{2h}^5$. With two molecules in the unit cell (as determined from the dimen-

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[1] A. A. Blanchard and W. L. Gilliland, J. Am. Chem. Soc. 48, 872 (1926).
[2] S. Sugden, *The Parachor and Valency* (Albert Knopf, New York, 1930), p. 189.
[3] L. Pauling, J. Am. Chem. Soc. 53, 1367 (1931); 54, 988 (1932).

[4] R. G. Dickinson, J. Am. Chem. Soc. 44, 2404 (1922).
[5] S. Sugden, J. Chem. Soc. 1932, 246. H. Covell and S. Sugden, ibid. 1935, 621.
[6] Tschugaeff, J. Russ. Phys. Chem. Soc. 42, 1466 (1910).
[7] H. Brasseur, A. de Rassenfosse and J. Pierard, Zeits. f. Krist. 88, 210 (1934). H. Brasseur and A. de Rassenfosse, Mem. Soc. Sci. Liége. [3] 18, 1 (1933).
[8] E. G. Cox, F. W. Pinkard, W. Wardlaw and K. C. Webster, J. Chem. Soc. 1935, 459.

sions of the unit and the density) the molecule is required to have a center of symmetry. This is possible only if the molecule is planar with a trans-configuration of the two salicylaldoxime groups. Robertson[9] has similarly investigated the nickel derivative of phthalocyanine and found that the molecule has a center of symmetry, which requires a planar configuration of the four bonds to the nickel atom.

For the case of nickel carbonyl the zero electric moment observed by Sutton and Bentley[10] indicates that the molecule must have either the square or tetrahedral configuration (with the carbonyl groups collinear with the nickel-carbon bonds) as opposed to a cyclic arrangement. These authors favored the tetrahedral configuration on the basis of Pauling's prediction.

The Raman and ultraviolet absorption spectra of nickel carbonyl have been studied by Dadieu and Schneider,[11] Anderson,[12] Thompson and Garratt,[13] and Duncan and Murray.[14] The first two investigators pointed out that the almost identical frequency of vibration of the carbonyl groups in nickel carbonyl and the carbon monoxide molecule is strong evidence for an identical structure of the carbon-oxygen bond in the two cases. Duncan and Murray investigated both the Raman and ultraviolet absorption spectra as well as the vibrations of a mechanical model of a square planar molecule. They ascribe incorrectly to Pauling a prediction of the square configuration for nickel carbonyl. From the fair agreement between their assignment of the frequencies in the spectra and the frequencies observed in the model and from a calculation of the symmetry number they conclude that the plane square model is correct or at least more probable than the tetrahedron. Wilson[15] points out that the failure of Duncan and Murray to observe the selection rules in assigning the observed frequencies to modes of vibration of

the molecule has led to an incorrect assignment of the frequencies; hence, their conclusions are invalidated.

Laird and Smith[16] have recently redetermined the parachor value of nickel carbonyl but reached no conclusion concerning the configuration of the four bonds.

The present investigation was undertaken in the hope of obtaining decisive evidence on the structure of nickel carbonyl and determining the values of the interatomic distances, which would be useful in considering the types of bonds involved.

The sample of nickel carbonyl was obtained from the Eastman Kodak Company. This was vacuum distilled and pumped off while frozen with liquid air in order to remove carbon monoxide. The small residue of nickel hydroxide produced by hydrolysis was left behind in the distillation. The compound was photographed with the sample at room temperature with a diffraction point to film distance of 10.43 cm and with the use of electrons having a wavelength of 0.0606A.

The photographs show eight maxima with a characteristic appearance of the diffraction pattern. The first maximum is weak while the second and third are both very strong and very sharp. The fourth maximum is weak and lies close to the third while the minimum following is broad and well defined. The fifth maximum is strong and sharp with the sixth, seventh, and eighth rings falling off in intensity in regular order.

Quantitative estimates were made of the apparent intensities of the successive rings and these data were combined with the observed values of the function $(4\pi \sin \theta/2)/\lambda$ to obtain an atomic distribution curve in the manner described by Pauling and Brockway.[17] This curve, reproduced in Fig. 1, represents the average distribution of scattering power around the atoms in the molecule of nickel carbonyl. Since the electrons in the beam are scattered chiefly by their interaction with the atomic nuclei the positions of the maxima in the distribution curve represent internuclear distances in the

[9] J. M. Robertson, J. Chem. Soc. **1935**, 615.
[10] L. E. Sutton and J. B. Bentley, Nature **130**, 314 (1932). L. E. Sutton, R. G. A. New and B. Bentley, J. Chem. Soc. **1933**, 652.
[11] Dadieu and Schneider, Anz. Acad. Wiss. Wien, Math. Naturwiss. Klasse **68**, 191 (1931).
[12] J. S. Anderson, Nature **130**, 1002 (1932).
[13] H. W. Thompson and A. P. Garratt, J. Chem. Soc. **1934**, 524.
[14] B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).
[15] E. B. Wilson, Jr., J. Chem. Phys. **3**, 59 (1935).

[16] F. W. Laird and M. A. Smith, J. Am. Chem. Soc. **57**, 266 (1935).
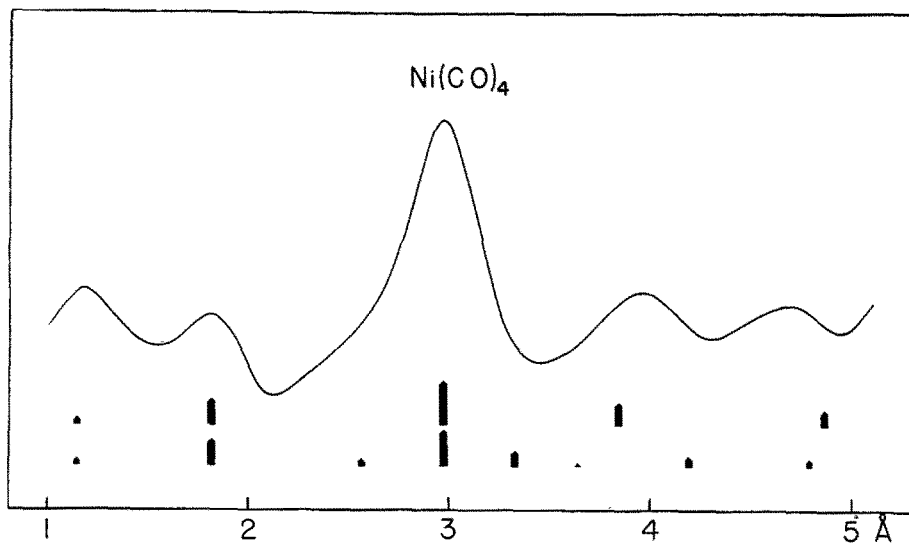[17] L. Pauling and L. O. Brockway, J. Am. Chem. Soc., in proof.

Fig. 1. Curve showing the observed radial distribution of scattering power in Ni(CO)$_4$. The two rows of arrows show the distances in the tetrahedral (upper) and square (lower) models based on the observed Ni—C and C—O distances.

molecule. Accordingly without any assumptions about the structure of the molecule we know that it must contain atomic separations near the values 1.18A, 1.82A, 2.97A, and 3.96A. This result may be combined with the usual procedure[18] for interpreting electron diffraction photographs in the consideration of square and tetrahedral arrangements of the atoms in nickel carbonyl.

The molecular models for which calculations of the theoretical intensity of electron scattering were made are alike in having four carbonyl groups joined to a central nickel atom with the line joining the carbon and oxygen atoms in the respective carbonyl groups passing through the central atom. This restriction is reasonable on the basis of a triple bonded carbon monoxide joined by a single bond to the nickel atom. Models were included in which the oxygen atoms are attached to the nickel as well as those having carbon atoms adjacent to the nickel atom. In the square configuration the carbonyl groups are directed toward the corners of a square; in the tetrahedral arrangement they point to the

vertices of a regular tetrahedron. Calculations were made for each of these arrangements with the ratio of carbon-oxygen to nickel-carbon distances varying from 0.55 to 0.65. Five of these curves are shown in Fig. 2 in which the intensity of elastically scattered electrons (calculated with atomic scattering powers which are constant over the scattering angle) is plotted against $(4\pi \sin \theta/2)/\lambda$ with an assumed Ni—C separation of 2.00A to fix the horizontal scale.

The general qualitative appearance of the photographs is well reproduced by the tetrahedral curves in Fig. 2. The square models with a C—O/Ni—C ratio of 0.625 or greater are unsatisfactory because they would require the seventh maximum to be appreciably stronger than the sixth and they fail to show the subsidiary fourth maximum following the strong third maximum. For values of the ratio below 0.625 the fourth maximum appears at a position about halfway between the third and fifth whereas the fourth is observed on the photographs to be much closer to the third maximum.

The quantitative comparison is given in Table I. The first column of data is calculated from the measured ring diameters and the wave-length

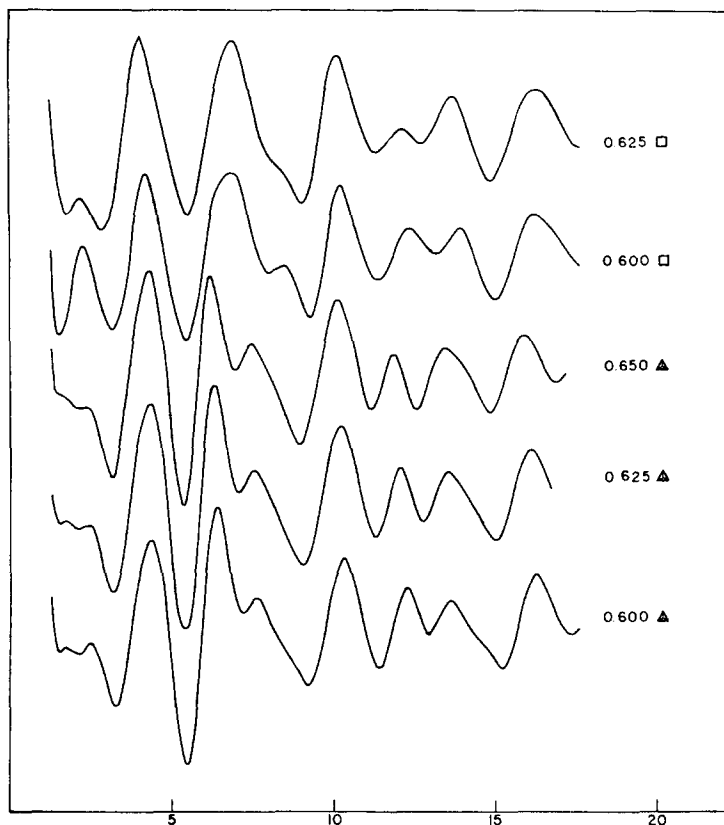[18] L. Pauling and L. O. Brockway, J. Chem. Phys. 2, 867 (1934).

FIG. 2. Theoretical intensity of electron scattering by Ni(CO)₄ with constant atomic scattering factors. The upper two curves correspond to square models and the lower three to tetrahedral models.

used. The second represents the visually estimated intensities used for the atomic distribution curve. The next five columns give the values of the indicated points on the theoretical curves, while the last five columns show the corresponding values for the size of the molecule in terms of the assumed distances. The assumed nickel-carbon separation of 2.00A is multiplied by the a values to give the experimentally determined values of the Ni—C distance. The C—O distance is then determined by means of the ratios used in the respective models.

The square models in the table are definitely inferior to the tetrahedral ones since they show an average deviation in the values for the size

of the molecule more than three times as great as that for the tetrahedral models. An even more serious discrepancy is found in the deviation of the value calculated from the fourth maximum. This maximum is subject to the St. John effect,[19] in which the apparent position of an unsymmetric ring is shifted in the direction of the greater contrast. In this case the effect would lead to too low a value of the molecular size. It will be observed in the tetrahedral models that the value from the fourth maximum is around five percent below the average from other rings whereas in the only square model

[19] L. O. Brockway and F. T. Wall, J. Am. Chem. Soc. 56, 2374 (1934).

TABLE I.

MAX.	MIN.	$\dfrac{4\pi \sin\theta/2}{\lambda}$	INTENSITY	TETRAHEDRAL			SQUARE		TETRAHEDRAL			SQUARE	
				$x_{0.650}$	$x_{0.625}$	$x_{0.600}$	$x_{0.625}$	$x_{0.600}$	$a_{0.650}$	$a_{0.625}$	$a_{0.600}$	$a_{0.625}$	$a_{0.600}$
1		2.63	5										
2		4.86	10	4.30	4.32	4.34	4.05	4.18	0.885	0.889	0.893	0.833	0.860
	3	5.92		5.35	5.38	5.43	5.50	5.45	.904	.909	.917	.929	.921
3		6.92	10	6.23	6.30	6.38	6.87	6.80	.901	.911	.922	.993	.983
	4	7.74		6.96	7.05	7.15		8.00	.900	.911	.924		1.034
4		8.70	6	7.45	7.55	7.60		8.45	(.856)	(.868)	(.874)		.972
	5	9.96		8.97	9.05	9.20	9.03	9.27	.900	.908	.924	.906	.931
5		11.09	7	10.12	10.25	10.35	10.10	10.20	.913	.924	.934	.911	.920
	6	12.14		11.20	11.30	11.40	11.35	11.38	.923	.931	.939	.935	.938
6		13.17	3	11.86	12.08	12.25	12.10	12.32	.901	.918	.930	.919	.936
	7	14.08		12.58	12.77	12.92	12.74	13.15	.894	.907	.918	.904	.934
7		15.01	2	13.45	13.58	13.64	13.65	13.83	.896	.904	.908	.909	.921
	8	16.25		14.85	15.05	15.20	14.85	15.00	.914	.926	.936	.914	.923
8		17.38	2	15.90	16.12	16.25	16.25	16.22	.915	.928	.935	.935	.934
								Average	.904	.914	.924	.917	.939
								Ave. Dev.	.007	.007	.007	.023	.027

Final Value Ni−C = 1.82±0.03A   Ni−C   1.808   1.828   1.848
C−O = 1.15±0.02A   C−O   1.175   1.142   1.109
Tetrahedral arrangement of atoms

which shows the fourth ring at all the value is four percent too high. Since the deviation is in the wrong direction it can be ascribed only to the unsatisfactory character of the square model.

Among the tetrahedral models we eliminate those having a ratio below 0.625 since they give values for the C−O distance lower than that observed in carbon monoxide. Since carbon monoxide is observed to have the triple bond distance, there is no form of covalent bond which could exist between the carbon and oxygen atoms in nickel carbonyl which would have a smaller interatomic distance. The effect on the triple bond itself of forming the extra bond to the nickel atom could scarcely be that of strengthening the bond and shortening the distance. Accordingly, we take the observed distance in carbon monoxide, 1.14A, as the lower limit for the carbon-oxygen separation in nickel carbonyl.

An upper limit on the C−O/Ni−C ratio may be placed at 0.65 since in models above that value of the ratio, some of the qualitative intensity comparisons occur in the wrong direction (such as seventh maximum greater than sixth). Accordingly we choose as most probable the tetrahedral model with a ratio of 0.63 and having Ni−C = 1.82±0.03A and C−O = 1.15 ±0.02A.

Inspection of the atomic distribution curve now leads to its interpretation in the light of the foregoing result. The vertical arrows in Fig. 1 show all of the interatomic distances in a tetra- hedral and a square molecule, respectively, of nickel carbonyl which has the Ni−C and C−O distances given above. The height of the arrows is proportional to the products of the scattering powers of the respective pairs of atoms. The large, sharp maximum at 2.97A corresponds to the Ni−O and the C−C distances which coincide in the tetrahedral model. The hump at 1.82A is the Ni−C separation. The less reliable hump for C−O appears at 1.18A but it should be observed that the difference between Ni−O and Ni−C is just 1.15A.

The atomic distribution curve also corroborates our choice of the tetrahedral arrangement. In the experience of Pauling and Brockway[17] the three distances in the square model at 2.57A, 2.97A, and 3.33A would not combine to give the sharp maximum observed at 2.97A.

Two practically independent methods of treating the electron diffraction photographs thus lead to the conclusion that nickel carbonyl is a tetrahedral molecule with the dimensions given above.

DISCUSSION

The observed carbon-oxygen distance, 1.15A, agrees with the value for carbon monoxide molecule and thus supports the previous evidence for a similarity of bonding in the carbonyl group in this compound and carbon monoxide. Since the latter compound is known[20] to resonate

[20] L. Pauling, J. Am. Chem. Soc. 54, 1000 (1932).

between the double bond and triple bond structures the question of finding this same state in nickel carbonyl is raised. With a triple bond between carbon and oxygen only a single electron pair bond could be formed between nickel and carbon as indicated in the first of the following structures. The formal charges are obtained by
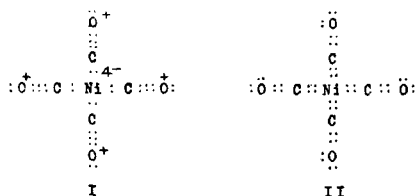
dividing the electrons in the bond and they indicate the directions of the semipolar bonds (sometimes represented by arrows). The nickel-carbon distance is observed to be 0.18A smaller than the sum of the covalent single bond radii. It is improbable that the nickel radius is in error by this amount or that the single bond would be shortened that much by its semipolar character (in spite of the rather large negative charge on the nickel atom); accordingly, it is suggested that this shortening is produced by resonance with the structure II in which all of the bonds are represented as double electron pair bonds. This represents an extreme state since the four bonds would perhaps not assume this character all at the same time. The double bonds are formed by placing two unshared pairs on oxygen and bringing one of the unshared pairs

of $3d$ electrons on nickel into the nickel-carbon bond. Since both the electrons and eigenfunctions are available, nickel does not share with the elements of the first row in the periodic table the restriction to four electron pair bonds. Structure II gives each atom a zero formal charge. Resonance between I and II explains the observed shortening of the nickel-carbon bond and allows the carbon-oxygen bond to exhibit a similar resonance between the double and triple states which it shows in carbon monoxide. For each of the bonds in nickel carbonyl the stronger of the resonating components determines the distance.

The directional properties[3] of structure I are determined by the fact that all five of the $3d$ eigenfunctions of neutral nickel are probably occupied by unshared pairs and the $4s$ and three $4p$ functions used in forming the four single bonds have the usual tetrahedral arrangement. For structure II no prediction can be made since the problem of four double bonds formed from d^4sp^3 has never been studied. Since structure I probably predominates in the resonance it is likely that its directional properties determine those of the normal state of the molecule; but in fact the observed tetrahedral configuration cannot be used as a criterion for the proposed resonance. It should again be noted that although this is the first definitely tetrahedral configuration observed in quadricovalent nickel compounds all of the other substances studied have been compounds of divalent nickel ion.