545. *The Structure of Nickel Tetracarbonyl and Some Disubstituted Derivatives.*

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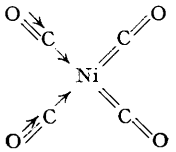
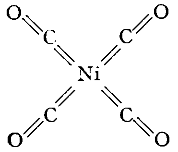
The structure of nickel tetracarbonyl is discussed. The infra-red spectrum and bond-length data are shown to be more compatible with a structure involving four Ni–C double bonds than with the generally accepted structure of two double bonds resonating among four positions. The stretching force constants of the C–O bonds in two disubstituted nickel carbonyls (*o*-phenylenebisdimethylarsinedicarbonylnickel^0 and dipyridyldicarbonylnickel^0) have been calculated from the infra-red frequencies. Consideration of these leads to the conclusion that the metal–ligand bonds in these complexes possess considerable double-bond character.

In order to explain the properties of certain transition-metal complexes it has been suggested that metal–ligand bonds may possess double-bond character (see, *e.g.*, Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1948, 2nd edn., p. 250; Chatt, *Nature*, 1950, **165**, 637; *J.*, 1952, 4300; Nyholm, *J.*, 1952, 2906; and for more detailed references see Nyholm, *J.*, 1951, 3245). Direct physical evidence on the point is difficult to obtain, but it was thought that observation of the bond-stretching force constants of the carbonyl bonds remaining when one or more of the carbonyl groups in nickel tetracarbonyl are replaced by other ligands would probably allow the nature of the metal–ligand bond to be inferred.

The vibrational spectrum of nickel tetracarbonyl was studied by Crawford and Cross (*J. Chem. Phys.*, 1938, **6**, 525), who reported a value of $15{\cdot}89 \times 10^5$ dynes cm.$^{-1}$ for the carbonyl bond-stretching force constant; they concluded that, since this value lies between the values associated with the C–O double bond in formaldehyde ($12{\cdot}1 \times 10^5$) and the triple bond in carbon monoxide ($18{\cdot}6 \times 10^5$ dynes cm.$^{-1}$), the nickel tetracarbonyl C–O bonds have partial triple-bond character. The structure of this compound was regarded therefore as a resonance hybrid of structures such as (I). The fact that the carbonyl force constants of nickel tetracarbonyl and carbon dioxide ($15{\cdot}5 \times 10^5$; Herzberg, "Infra-red and Raman Spectra," Van Nostrand, N.Y., 1945, p. 187) are very similar was also noted.



(I)



(II)

The validity of comparison of the force constants of nickel tetracarbonyl and formaldehyde must be questioned, since the σ-bonds formed by the carbon atoms in those two cases are of different types. In formaldehyde the carbon bonds are sp^2 (trigonal) hybrids, while in nickel tetracarbonyl, for which the Ni–C–O groups are linear (Sutton, New, and Bentley, *J.*, 1933, 652; Ladell, Post, and Frankuchen, *Acta Cryst.*, 1952, **5**, 795), the carbon bonds are *sp* hybrids. It is known that increase in the proportion of *s* to *p* character in the carbon bonds is accompanied by an increase in bond strength (Sutherland and Dennison, *Proc. Roy. Soc.*, 1935, *A*, **148**, 250; Walsh, *J.*, 1948, 398; Maccoll, *Trans. Faraday Soc.*, 1950, **46**, 359).

Few compounds are available having a carbonyl group of which the carbon has *sp* hybridisation, and these are such that simple conclusions about their structure are difficult to reach. Carbon dioxide and carbonyl sulphide have C–O bond-stretching force constants of 15·5 and $14{\cdot}2 \times 10^5$ dynes cm.$^{-1}$, respectively (Herzberg, *op. cit.*, pp. 174, 187). Pauling (*op. cit.*, p. 197) has explained the bond lengths in these compounds as being due to resonance involving partial triple-bond character. If it be recognised that bond characteristics depend on the hybridisation of the σ-bonds involved, the importance of such resonance is much diminished. For example, a C–O bond length of about 1·15 Å and force constant of $15{\cdot}5 \times 10^5$ dynes cm.$^{-1}$ appear to be characteristic of a normal double bond involving *sp* hybrid σ-bonds. On this basis carbon dioxide may be represented satisfactorily as O=C=O (Coulson, "Valence," O.U.P., 1952, p. 211). A further example of this type of carbonyl bond is afforded by keten ($CH_2{=}C{=}O$) in which the C–O bond length is 1·17 Å (Beach and Stevenson, *J. Chem. Phys.*, 1938, **6**, 75). Halverson and Williams (*ibid.*, 1947, **15**, 552) give a set of force constants for keten including $15{\cdot}5 \times 10^5$ dynes cm.$^{-1}$ for the carbonyl bond stretching constant, which can be used to calculate the A_1 vibration frequencies to within 2%. However, since there are only four frequencies (*A* species) and at least five force constants, *viz.*, C=O stretching ($K_{C=O}$), C=C stretching ($K_{C=C}$), C–H stretching (K_{C-H}), CH_2 bending ($K_{\delta CH_2}$), and C=C=O interaction (k), are required for a reasonable representation of the vibration characteristics, some doubt must arise as to the best value for any of these constants. For example, a set of possible constants given by Harp and Rasmussen (*ibid.*, p. 778), in which $K_{C=O}$ is $13{\cdot}43 \times 10^5$ dynes cm.$^{-1}$, when used to calculate the frequencies of the A_1 vibrations by the method used by Halverson and Williams gave the results shown below, in which the agreement with the observed values is

	Frequencies : *				Frequencies : *		
Vibration	Calc. (1)	Calc. (2)	Obs.	Vibration	Calc. (1)	Calc. (2)	Obs.
CH	3045	3046	3066	C=C	1086	1037	1120
C=O	2133	2168	2153	CH_2	1409	1354	1386

* (1) By using $K_{C=O} = 15{\cdot}5$, $K_{C=C} = 9{\cdot}8$, $K_{CH} = 5{\cdot}23$, $k = 1{\cdot}5$ ($\times 10^5$ dynes cm.$^{-1}$), $K_{\delta CH_2}$ $0{\cdot}494 \times 10^{-11}$ erg/radian^2.

(2) By using $K_{C=O} = 13{\cdot}43$, $K_{C=C}$ 9·7, $K_{CH} = 5{\cdot}23$, $k = -0{\cdot}12$ ($\times 10^5$ dynes cm.$^{-1}$), $K_{\delta CH_2} = 0{\cdot}494 \times 10^{-11}$ erg/radian^2.

almost as good as that obtained when Halverson and Williams's force constants were used. It seems reasonably certain nevertheless that the carbonyl bond in keten has very similar characteristics to those of carbon dioxide and carbonyl sulphide.

There is obtained in this way considerable support for the belief that nickel tetracarbonyl with C–O bond distance 1·15 Å (Crawford and Horawitz, *J. Chem. Phys.*, 1948, **16**, 147) and bond-stretching force constant $15{\cdot}89 \times 10^5$ dyne cm.$^{-1}$ (Crawford and Cross, *ibid.*, 1938, **6**, 525) is best formulated as (II) in which the nickel atom forms double bonds with the four carbon atoms (cf. Coulson, *op. cit.*, p. 216). One of the difficulties associated with the acceptance of structure (I) is the fact that it requires a relatively high negative formal charge on nickel which is improbable for a metal (cf. Pauling, Victor Henri Memorial Volume, Liége, 1948, p. 4; *J.*, 1948, 1461). The second structure minimises such formal charge effects and, except for ionic character produced by the difference in electronegativity of the bonded atoms, leaves the nickel neutral. An extension of this work to other carbonyls should yield valuable results, iron pentacarbonyl being now under investigation. In the sequence $Ni(CO)_4 \longrightarrow Fe(CO)_5 \longrightarrow Cr(CO)_6$ the bond-length data * have been interpreted to mean that double-bond character is steadily decreasing. At first sight this is to be expected because (*a*) the number of $3d$ electrons available for π-bond formation is decreasing along the above sequence ($10 \longrightarrow 8 \longrightarrow 6$); and (*b*) the total number of bonds required is increasing ($4 \longrightarrow 5 \longrightarrow 6$). Unfortunately, the problem is complicated by the fact that the σ-bond hybridisation is also changing along the series ($sp^3 \longrightarrow dsp^3 \longrightarrow d^2sp^3$) and this should affect both force-constant and bond-length data.

If two of the carbonyl groups are replaced by the chelate group, *o*-phenylenebisdimethylarsine (III) = diarsine, to form *o*-phenylenebisdimethylarsinedicarbonylnickel^0 (IV) (Nyholm, *J.*, 1952, 2906), the carbonyl bond-stretching frequencies are found to be 1940 and 1996 cm.$^{-1}$ (for solution in tetrachloroethylene). The splitting of the carbonyl absorption into two bands is similar to that observed in nickel tetracarbonyl itself which gives rise to bands at 2043 and 2050 cm.$^{-1}$. Although it is not possible to carry out a complete analysis of the spectrum and so calculate an accurate value for the C–O bond-stretching force constant, an approximate value can be obtained on the assumption that the 1940 and 1996 cm.$^{-1}$ absorption bands arise from vibrations confined to the carbonyl groups. A correction can be applied for interaction with the Ni–C vibration, for which Crawford and Cross (*loc. cit.*) give the frequency of about 348 cm.$^{-1}$. The value calculated in this way for the C–O bond-stretching force constant ($15{\cdot}0 \times 10^5$ dynes cm.$^{-1}$) may still be a little higher than the true value but the error is probably less than $\pm 0{\cdot}3 \times 10^5$ dynes cm.$^{-1}$.

EXPERIMENTAL AND CALCULATION

The spectrum of (IV) was measured with a Perkin Elmer Model 12C Spectrometer, a sodium chloride prism being used. The C–O bond-stretching force constant (k) was calculated by means of the formula

$$k = 4\pi^2 \mathbf{c}^2 \nu^2 \mu_{CO} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (1)$$

where $\mathbf{c}$ = velocity of light, μ_{CO} = reduced mass of carbon and oxygen atoms, and ν = C–O bond stretching frquency, which is given by $\nu^2 = \frac{1}{2}(1940^2 + 1996^2)$. The effect of coupling of the C–O and Ni–C bond-stretching vibrations was estimated by using Matthieu's formula ("Spectres de Vibration et Symmetrie," Herman, Paris, 1947, p. 427), *viz.*,

$$\nu^2 = \nu^2_{CO}\left[1 + \frac{\alpha \nu^2_{Ni-C}}{\nu^2_{CO} - \nu^2_{Ni-C}}\right] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (2)$$

where, ν_{CO} and ν_{Ni-C} are the bond-stretching frequencies without coupling of the vibrations, ν = observed carbonyl bond-stretching frequency (showing effect of coupling with the Ni–C vibration), and α = coupling coefficient given by

$$\alpha = \mu_{CO} \times \mu_{NiC}/m^2_C$$

where μ_{CO} and μ_{NiC} are the reduced masses for the atoms concerned in the several vibrations and m_C = mass of the carbon atom. From (1), $k = 15{\cdot}7 \times 10^5$ dynes cm.$^{-1}$. Application of (2) gives $\nu_{CO} = 1928$ cm.$^{-1}$ if $\nu_{NiC} = 500$ cm.$^{-1}$. This high value of the Ni–C bond stretching frequency was chosen to give an estimate of the upper limit of the effect of interaction on the carbonyl frequency. Use of $\nu_{CO} = 1928$ cm.$^{-1}$ in formula (1) gives $k = 15{\cdot}0 \times 10^5$ dynes cm.$^{-1}$.

DISCUSSION

It is seen that replacement of two carbonyl groups by *o*-phenylenebisdimethylarsine to form the complex (IV) has had little effect on the character of the remaining two carb-

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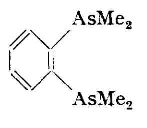
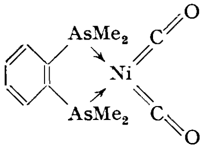
* The authors thank a Referee for raising this point.

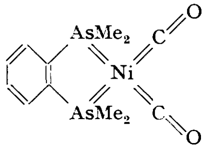
onyl bonds, which are very similar to those of nickel tetracarbonyl. Two possibilities arise for the basic structure of the diarsine (IV), *viz.*, (IV*a*), in which the arsenic forms co-ordinate bonds with the nickel, and (IV*b*), in which nickel and arsenic are doubly bonded. An important difference between these structures lies in the fact that, whereas in (IV*b*) the nickel atom is effectively neutral, yet in (IV*a*) it carries a negative formal charge. This could be dissipated through resonance with structures such as (IV*c*) which would have a considerable effect on the force constant of the carbonyl bond. It is concluded therefore that the most important structure for the diarsine complex is (IV*b*), in which the nickel forms double bonds with the arsenic.



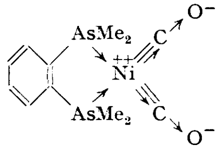
(III)



(IV*a*)



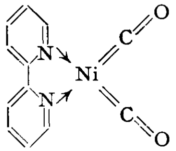
(IV*b*)



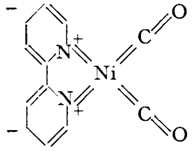
(IV*c*)

It is significant in this connection that only those ligands which are capable of double-bond formation (*e.g.*, tertiary arsines and phosphines, *iso*cyanides) have been observed to replace the carbonyl groups of nickel tetracarbonyl, and that no compounds have been reported of ligands for which it is not possible to write feasible double-bond structures.

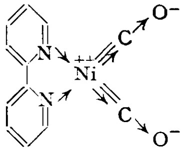
A similar investigation of the red dipyridyl complex (V) was attempted. Unfortunately, this compound is insoluble in solvents suitable for infra-red studies and had to be examined as a suspension in paraffin. Under these conditions the carbonyl frequencies were found to be 1861 and 1950 cm.$^{-1}$. Under similar conditions the frequencies for the diarsine were 1916 and 1977 cm.$^{-1}$, instead of 1940 and 1996 cm.$^{-1}$ when measured in dilute solution. If the frequencies of the dipyridyl complex are adjusted to allow for the effect of state as observed in the diarsine, and calculations are carried out as above, a C–O bond-stretching force constant of $14{\cdot}4 \times 10^5$ dynes cm.$^{-1}$ is obtained. This suggests that the bond order is a little lower than in the diarsine, as might be expected if structure (V*c*) contributed to the resonance hybrid. This might be expected to play a more important part than in the diarsine since Ni–N double bond formation necessitates a separation of charge in the ligand. This necessity for charge separation would certainly mean that a full double bond between the nitrogen and the nickel as in (V*b*) is improbable, and this structure would only make a partial contribution to the resonance hybrid; this should be contrasted with the arsine bond where a complete double bond is feasible. This conclusion that dipyridyl has a smaller capacity for double-bond formation than diarsine lends some support for the conclusions derived from magnetic measurements (Burstall and Nyholm, *J.*, 1952, 3570).



(V*a*)



(V*b*)



(V*c*)

The foregoing is considered to provide strong evidence for the postulate that in the above substituted nickel carbonyl complexes there is double-bond character in the Ni–As and Ni–N bonds. This conclusion supports the idea that double-bond character is possible in other metal–ligand bonds, as has frequently been suggested.

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