Catena-[μ-(o-phthaloyl-*C*,*C′*,*O*)]-μ-iodo-iodonickel(IV): Crystal and Molecular Structure

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Summary The crystal structure of the title compound, a linear polymeric nickel compound with alternate iodine and carboxyl bridges and incorporating the unique carbon-bonded (*o*-phthaloyl-*C* *C′*,*O*)$^{2-}$ tridentate ligand (I) has been determined

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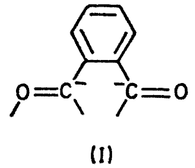
WHEN equimolar quantities of nickel carbonyl and *o*-di-iodobenzene are heated in a sealed tube for 1 h at 70° in cyclohexane as solvent, fine, black, acicular, diamagnetic crystals are readily obtained in high yield The product was originally reported to be π-benzyne-di-iodo-μ-carbonylnickel dimer[1] Further examination in these laboratories revealed that the material is insoluble in the preparative solvent and decomposes readily in those solvents in which it dissolves The decomposition products include iodine and derivatives of *o*-phthalic acid, for example on attempting to record the ^{1}H n m r spectrum in CD_3OD, the aromatic part of the spectrum was found to correspond to that of $C_6H_4(CO_2CD_3)_2$ (*cf* ref 1) The volatile products of pyrolysis at 400 and 700° were analysed by combined g l c -m s, and were found to be principally iodobenzene phthalic anhydride, and *o*-di-iodobenzene, together with smaller quantities of diphenyl ketone, fluorenone, and anthraquinone, volatile nickel products were not observed nor were any species with a strong peak at *m/e* 388 This latter peak is found in the straight mass spectrum of the compound,[1] but we have no satisfactory explanation for the ion involved Nevertheless, formulations which contained derivatives of the phthalate ion did not accord[2] with the strong i r peak at 1796 cm^{-1} (sh 1768 cm^{-1}) which was originally assigned to carbonyl groups that were bridging nickel atoms An *X*-ray investigation of one of the crystals was undertaken in order to resolve this dilemma



(I)

A crystal of length 0 25 mm was sealed in a thin-walled glass capillary tube, it was found to be monoclinic with $a = 9\ 52$ $b = 6\ 57$, $c = 16\ 99$ Å, $\beta = 109° 8'$ and space group $P2_1/c$ The observed density of the crystals was 2 95 g cm^{-3} which is in poor agreement with the value of

2·75 g cm^{-3} calculated on the basis of four molecules of $C_6H_4(CO)NiI_2$ in the unit cell. Three-dimensional *X*-ray data were collected on a Philips 'PAILRED' diffractometer; the 944 independent reflections with intensities exceeding 2·5 σ were corrected for Lorentz and polarisation effects but not for absorption, and were used for the solution of the structure. The positions of the iodine and nickel atoms were determined by examination of the Patterson function; the lighter atoms (excluding hydrogen atoms) were found by conventional Fourier methods. The structure has been refined to a current reliability factor of 0·082, treating the vibrations of the heavier atoms anisotropically and those of the lighter atoms isotropically.

The structure of this unusual compound is shown in the Figure. The molecule contains one additional carbonyl group per nickel atom as compared with the original formulation. Analytical results are scarcely sensitive enough to distinguish between the original formulation and that determined; $C_6H_4(CO)_2NiI_2$ requires C 21·6, H 0·90, I 57·2%; values determined were C 20·8, H 1·03, I 56·1%. The revised formula also gives a calculated density of 2·94 g cm^{-3} which is excellent agreement with observation.

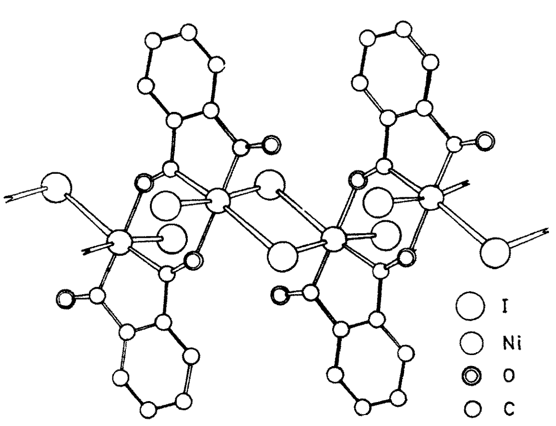


FIGURE. *Four units of the molecular structure of catena-*[μ-(o-*phthaloyl*-C,C′,O)]-μ-*iodo-iodonickel*(iv).

The compound contains a number of unusual features: the chains of nickel atoms, which are parallel to the crystallographic *b* axis, are bridged by alternate centrosymmetric iodine and carboxyl bridges; each nickel atom is six-co-ordinate. An unique feature of the compound is the five-membered chelate ring formed with the (*o*-phthaloyl-*C,C′,O*)$^{2-}$ ligand which is bonded through the ketonic *carbon* atoms. This system may, alternatively, be regarded as an *o*-phenylene group linked to a nickel atom by two carbonyl bridges; this latter picture correlates with the method of preparation which may, indeed, have involved the very reactive benzyne intermediate obtained by thermal decomposition of *o*-di-iodobenzene. The bridging-carbonyl i.r. frequencies are intermediate between the regions conventionally associated with carbonyl groups bridging metal atoms and those in organic systems. The other two co-ordination sites in this plane are occupied by an iodine atom bridging to an adjacent nickel atom and by an oxygen atom from the (*o*-phthaloyl-*C,C′,O*)$^{2-}$ group which is attached to the other adjacent nickel atom. The two remaining co-ordination sites are taken up by the second bridging iodine atom and by a terminal iodine atom. The six-membered carboxyl bridge system is essentially co-planar with the (*o*-pthaloyl-*C,C′,O*)$^{2-}$ groups and is perpendicular to the iodine bridge system.

Distances and angles within the *o*-phenylene group are similar to those in *o*-phthalic acid and its mono-anion.[3,4] The C–O bond length of the simple bridging carbonyl group is 1·14 Å, compared with 1·23 Å in the organic acid, 1·30 Å for the bridging carbonyl groups of $Fe_2(CO)_9$, and 1·15 Å for the terminal groups of $Fe_2(CO)_9$ and $Ni(CO)_4$.[5,6] The bond length of 1·17 Å for the bridging carboxyl group is not significantly greater (at the current stage of refinement) than that for the simple bridging carbonyl group; it is, however, substantially shorter than that observed by Lindley and Mills for the bridging carboxyl group (1·26 Å) in the compound $(CO)_3\cdot Fe[\mu\text{-}C(C_6H_5)O]_2\cdot Fe(CO)_3$.[7] Furthermore, the six-membered carboxyl bridge system in this iron compound adopts a boat conformation whereas the corresponding bridge system in the present compound is almost planar: this planar arrangement is not demanded by any other structural features and suggests some sort of 'aromatic character' for the ring. The metal–oxygen distance of 2·15 Å is similar to those found for $Ni–OH_2$ in nickel sulphate, acetate, salicylaldehydate and acetylacetonate,[8] but a little longer than the nickel–oxygen bonds to the chelates. Likewise, the nickel–carbon bonds (1·90 and 1·94 Å) are longer than those in $Ni(CO)_4$ (1·84 Å),[6] also than the $Fe–C_t$ bonds in $(CO)_3\cdot Fe[\mu\text{-}C(C_6H_5)O]_2\cdot Fe(CO)_3$[7] (mean value 1·81 Å); they more closely resemble the Fe–carboxyl bond in this latter compound (1·95 Å). The length of the bond to the terminal iodine atom (2·51 Å) agrees closely with the sum of covalent radii; the mean $Ni–I_\mu$ distance (2·66 Å) is 0·15 Å greater than the $Ni–I_t$ value. The iodine bridge is strikingly asymmetric, the lengths being $Ni–I_\mu$ (*trans* to I) 2·55 Å, $Ni–I_\mu$ (*trans* to C) 2·77 Å; this suggests that the (*o*-phthaloyl-*C,C′,O*)$^{2-}$ ligand exerts a very strong *trans*-influence. This observation may be in keeping with the comparatively long nickel–carbon and nickel–oxygen distances and with the short carbon–oxygen distances of this compound, which may add an unusual electronic arrangement to its novel structure.

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