recent single crystal studies of $Co[Hg(SCN)_4]$,[25] $[Cu(en)_2][Hg(SCN)_4]$[24] and $K_2[Co(NCS)_4 \cdot 4H_2O$.[26] The orientation of the linear NCS radicals in each of the lattices is such that the nearest neighbors of Hg are S atoms while the nearest neighbors of Co in each case are N atoms.

If the parent cations are assumed to have the isothiocyanato structure, it appears from this study that a Hg(II) ion (and to a less degree a Ag(I) ion) may interact with the highly polarizable sulfur of either one or two thiocyanato groups. One may speculate that the bonds formed make use of the co-linear s or sp hybrid orbitals of dicovalent Hg(II) plus sp orbitals of the sulfur, the latter directed at large angle to C–S (*viz.*, 100–130°).

The picture of the 1:1 and 2:1 interaction species involving the monothiocyanatopentaammines is straightforward. Further, the especially stable 1:1 soluble species involving *cis*-dithiocyanato cations suggest the presence of rings involving one or two Hg(II) or Ag(I) ions, respectively, bonding the sulfurs of one or two dithiocyanato cations, while the slightly soluble, less stable 2:1 species possibly consists of a dichelate cation having the four sulfurs tetrahedrally bonded to a single Hg(II) ion. The very much smaller solubilities of the *trans*-dithiocyanatobis-(ethylenediamine) interaction species may be attributed to a tendency of the *trans* structures to form insoluble polymeric chains involving alternate links of complex and metal cations.

The isolation and characterization of solids was not a prime objective in these studies since we were concerned with the nature of the thiocyanato complex–metal interaction cations associated with the color changes observed in solution. Preliminary experiments with the monothiocyanatopentaammines and Ag(I) and Hg(II) indicated that the empirical composition, crystal form and homogeneity of the products isolated were sensitive to conditions such as temperature and concentration of constituents. It appears possible from the observed weak nature of these interactions that the ions which exist in solution bear no direct relation to (and therefore cannot be inferred from) the crystalline isolates. However, such might well constitute a separate study in itself.

In conclusion, the interaction of a thiocyanato complex cation with either Ag(I) or Hg(II) cations is rather unique in type. Perhaps the closest analogy is found in the addition of hydrogen ion to a hydroxo or carbonato cation (*e.g.*, $[Co(NH_3)_5OH]^{+2}$ or $[Co(NH_3)_5CO_3]^{+1}$) to form the corresponding aquo or hydrocarbonato cation. The blue shift which is observed in the absorption of the parent complex upon adding acid is immediate and quite similar to the shift observed, for example, in a solution containing $[Co(NH_3)_5NCS]^{+2}$ in the presence of Ag(I) or Hg(II) cations. Further analogy is seen in the effect of the central atom. Just as $[Co(NH_3)_5OH]^{+2}$ has a greater affinity than $[Cr(NH_3)_5OH]^{+2}$ for hydrogen ion[27] similarly $[Co(NH_3)_5NCS]^{+2}$ interacts more strongly than $[Cr(NH_3)_5NCS]^{+2}$ with either silver or mercuric ions.

Acknowledgment.—One of us (W.C.W.) gratefully acknowledges the encouragement and interest of Dr. R. W. Stoughton, Oak Ridge National Laboratory, during the latter phase of this work.

OAK RIDGE, TENN.

---

[25] J. W. Jeffery, *Nature*, **159**, 610 (1947).

[26] G. S. Zhdanov and Z. V. Zvonkova, *Zhur. Fiz. Khim.*, **24**, 1339 (1950); *cf. C. A.*, **45**, 6001e (1951).

[27] K. Glen and W. Cuntze, *Z. anorg. allgem. Chem.*, **237**, 187 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Mixed Ligand Complexes of Nickel(II) with Cyanide and 1,10-Phenanthroline

BY ALFRED A. SCHILT

RECEIVED DECEMBER 17, 1958

Attempts to prepare the conceivable mononuclear mixed ligand complexes of nickel(II) with cyanide and 1,10-phenanthroline (ophen) did not yield any of the anticipated products but resulted instead in the isolation of three different complex compounds. The empirical formulas of these insoluble substances are Ni_2 $ophen_3(CN)_4(H_2O)_4$, Ni $ophen(CN)_2(H_2O)$ (a yellow solid) and Ni $ophen(CN)_2(H_2O)_{0.5}$ (a lavender solid). Chemical, spectrophotometric and magnetic data indicate the identity of the first to be $[Ni\ ophen_3][Ni(CN)_4] \cdot 4H_2O$; the latter two are mixed ligand complexes which, in view of their peculiar properties, may involve cyanide bridging groups.

Introduction

Coördination of bivalent nickel by 1,10-phenanthroline gives rise to a paramagnetic octahedral complex; whereas in the case of cyanide coördination a diamagnetic square coplanar complex of nickel(II) results.[1] It is therefore of interest to learn whether or not one or more complexes of nickel(II) can be obtained which involve both of these very dissimiliar coördinating groups. If any mixed ligand complexes of nickel(II) with cyanide and 1,10-phenanthroline do exist, it is anticipated that their properties may prove to be of unusual interest in regard to possible applications and theoretical significance.

Previous studies have revealed the existence, identities and properties of the mixed ligand complexes of iron(II) with cyanide and 1,10-phenanthroline.[2–4] The peculiarities observed for this series of mixed ligand complexes together with

---

[1] R. S. Nyholm, *Chem. Revs.*, **53**, 263 (1953).

[2] G. A. Barbieri, *Atti. accad. Lincei*, **20**, 273 (1934).

[3] A. A. Schilt, THIS JOURNAL, **79**, 5421 (1957).

[4] J. Bjerrum, A. W. Adamson and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956).

the considerations set forth above for nickel(II) led to the present investigation.

Experimental

Preliminary Studies.—The aqueous system with components nickel acetate, 1,10-phenanthroline, potassium cyanide, acetic acid and sodium acetate was examined for the formation of insoluble or colored products. Formal concentrations of the added components were varied in a manner designed to provide for or encourage the production of the following conceivable mixed ligand complexes[5]: [Ni $\text{ophen}_2(\text{CN})_2$], [Ni $\text{ophen}(\text{CN})_4]^=$, [Ni $\text{opehn}(\text{CN})_2$]. Different concentration ratios of acetic acid to acetate ion were employed to vary the *p*H and therewith the degree of competition between cyanide ions and 1,10-phenanthroline for coördination with nickel(II). The order of mixing was also considered in the event that one type of substitution reaction were more favorable than another. These studies led to the discovery of and suitable preparatory conditions for the compounds herein described.

Preparation of Compounds. A. [Ni ophen_3][Ni$(\text{CN})_4$]·$4H_2O$.—A freshly prepared solution of 0.4 g. of KCN (0.006 mole) in 10 ml. of water was added slowly with stirring to a hot solution of 0.74 g. of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ (0.0030 mole) and 1.2 g. of 1,10-phenanthroline monohydrate (0.0060 mole) in 200 ml. of water. A white amorphous precipitate formed at first, but this rapidly changed color to rose-red during the addition of the remaining KCN solution. The precipitate was digested for several minutes near boiling temperature before it was isolated by suction filtration and washed with distilled water. Recrystallization from ethanol-water (1:1 by volume) gave a rose-red crystalline product which was dried in air at room temperature; yield 75%.

Anal. Calcd. for [Ni ophen_3][Ni$(\text{CN})_4$]·$4H_2O$: C, 57.59; H, 3.87; N, 16.80; Ni, 14.07; H_2O, 8.63. Found: C, 58.11; H, 3.54; N, 16.96; Ni, 14.19; H_2O, 7.4.

B. Yellow Ni ophen$(\text{CN})_2(H_2O)$.—The blue colored solution obtained on dissolving 1.99 g. of $Ni(C_2H_3O_2) \cdot 4H_2O$ (0.0080 mole) and 1.60 g. of 1,10-phenanthroline monohydrate (0.0080 mole) in 200 ml. of an aqueous solution containing 20 ml. of glacial acetic acid and 30 g. of sodium acetate was cooled in an ice-bath. A freshly prepared solution of 1.1 g. of KCN in 10 ml. of water was added slowly with stirring to the ice-cold solution. The yellow, finely divided, amorphous precipitate which formed was aged 1 hr. in the ice-bath, collected by suction filtration, washed several times with cold distilled water and dried in air; yield 60%. Although a higher yield is attainable, it was avoided in order to minimize any possibility for contamination by other insoluble cyanide salts. Such was assumed to be desirable since no solvent for recrystallization of the product could be found.

Anal. Calcd. for Ni ophen $(\text{CN})_2(H_2O)$: C, 54.4; H, 3.23; N, 18.1; Ni, 19.0; H_2O, 5.8. Found: C, 53.2; H, 3.35; N, 19.0; Ni, 18.8; H_2O, 4.7.

C. Lavender Ni ophen$(\text{CN})_2(H_2O)_{0.5}$.—The blue colored solution obtained on mixing 1.99 g. of Ni $(C_2H_3O_2) \cdot 4H_2O$ (0.0080 mole), 1.60 g. of 1,10-phenanthroline monohydrate (0.0080 mole), 20 ml. of glacial acetic acid and 180 ml. of distilled water was heated on a steam-bath. A freshly prepared solution of 1.1 g. of KCN in 10 ml. of water was added slowly with stirring. The color of the amorphous precipitate which separated out during this addition changed rapidly from yellow to white and then gradually to lavender on further heating. After a digestion period of several hours on the steam-bath the lavender colored precipitate was collected by suction filtration, washed with distilled water and dried in air. A yield of 1.6 g. was obtained. No solvent could be found which was suitable for recrystallization of the product. Since purification was not feasible, the yield was purposely kept low to discourage any tendency for contamination by other insoluble cyanide salts.

Anal. Calcd. for Ni ophen$(\text{CN})_2(H_2O)_{0.5}$: C, 56.1; H, 3.00; N, 18.7; Ni, 19.6; H_2O, 3.0. Found: C, 55.4; H, 3.01; N, 19.7; Ni, 19.6; H_2O, 1.9.

Analyses.—Water was determined as the loss in weight on drying at 197° *in vacuo* over phosphorus pentoxide. For the determination of nickel each sample was first ignited to destroy organic matter; the ignition residue was dissolved in hydrochloric acid and nickel was then separated and weighed as nickel dimethylglyoxime.

Carbon, hydrogen and nitrogen analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Magnetic Measurements.—The magnetic susceptibilities of the solid samples were determined by the Gouy method using water and ferrous ammonium sulfate hexahydrate as calibration standards. Measurements were made at room temperature (25–27°) only. Values of molar susceptibility given in column 2 of Table I are for the complex; the values in column 3 have been corrected for the diamagnetisms of ligands. Diamagnetic corrections used are: cyanide ion -13×10^{-6},[6] 1,10-phenanthroline -119×10^{-6},[7] water -13×10^{-6}.[7]

TABLE I

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF SOLID COMPLEXES

Compound	$X_m \times 10^6$ (complex)	μeff. (nickel ion)
[Ni ophen_3][Ni$(\text{CN})_4$]·$4H_2O$	+4454 ± 90	2.19
Lavender Ni ophen$(\text{CN})_2(H_2O)_{0.5}$	+2291 ± 30	2.26
Yellow Ni ophen$(\text{CN})_2(H_2O)$	+1002	1.67
Yellow Ni ophen$(\text{CN})_2$	+1056	1.70

Infrared Spectra.—Compounds were examined as solids in Nujol mulls using a Perkin–Elmer Model 21 recording spectrophotometer. Infrared spectra were determined in the frequency range 650–4000 cm.$^{-1}$. The absorption frequencies are listed in Table II.

Results and Discussion

Substitution reactions between tris-(1,10-phenanthroline)-nickel(II) and cyanide ions might be expected to give rise to the mixed ligand complexes [Ni $\text{ophen}_2(\text{CN})_2$] and [Ni $\text{ophen}(\text{CN})_4]^=$ in a manner analogous to that for the iron(II) series of mixed complexes with such ligands.[3] However, no evidence for the formation of either of these complexes was revealed by the methods employed in the present study. Cambi, Cagnasso and Tremolada report isolation of Ni $\text{ophen}_2(\text{CN})_2$ from $Ni(\text{CN})_2$ and excess 1,10-phenanthroline in alcohol–water[9]; no detailed information was presented. Attempts by the present investigator to confirm this observation were unsuccessful.

Consideration of conceivable complexes which might arise, on the other hand, from substitution reactions between tetracyanonickelate(II) ions and 1,10-phenanthroline leads to only one mononuclear species, *i.e.*, the neutral [Ni $\text{ophen}(\text{CN})_2$] complex. During this investigation two distinctly different compounds having the empirical formula Ni $\text{ophen}(\text{CN})_2$ were isolated, but neither exhibit certain of the properties expected for the above complex.

Because of the strong affinity of nickel ions for either cyanide ions or 1,10-phenanthroline and on the basis of solubility considerations, one would expect the formation and isolation of the neutral complexes [Ni $\text{ophen}_2(\text{CN})_2$] and [Ni $\text{ophen}(\text{CN})_2$] to be favorable. Failure to obtain either of these

---

(5) The complexes cited above by formula (ophen represents 1,10-phenanthroline) are the possible non-bridged complexes of 4- and 6-covalent nickel(II) in which only cyanide and bidentate 1,10-phenanthroline ligands are involved.

(6) P. W. Selwood. "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 36.

(7) Ref. 6, pp. 51–52.

(8) Ref. 6, p. 28.

(9) L. Cambi, A. Cagnasso and E. Tremolada, *Gazz chim. ital.*, **64**, 758 (1934).

TABLE II

FREQUENCIES, CM.$^{-1}$, OF INFRARED ABSORPTION BANDS FOR SOME NICKEL(II) COMPLEXES

The more intense bands are designated by asterisks.*

[Ni ophen$_3$] [Ni(CN)$_4$]·4H$_2$O	Yellow Ni ophen (CN)$_2$(H$_2$O)	Lavender Ni ophen (CN)$_2$(H$_2$O)$_{0.5}$
	2330	2320
	2170	2170
	2155	2152*
2125*	2138*	2130
1628	1630	1627
1607	1615	1606
1585	1588	1590
		1585
1520*	1524*	1520*
1498	1502	1499
1432*	1443	1428
	1433	
1338	1348	1346
1306	1311	1307
	1237	
1225	1227	1226
1212	1210	1215
		1199
	1154*	1152
1142	1150	1144
	1118	
1105	1108	1107
	1100	1095
	1056	1056
	1042	1042
870	963	961
862	884	
847	873	871
845*	858*	850*
	852	
	793	778
762	775	773
728	752	
724*	728*	726*
	722	

suggests that a configuration involving coördination of 1,10-phenanthroline together with exactly two cyanide ligands about bivalent nickel is decidedly unstable. Inasmuch as the [Ni ophen(CN)$_4$]$^=$ species also could not be detected, it appears that this configuration is also unfavorable. However, a more convincing argument against such a structure lies in the consideration that the four cyanide ligands would undoubtedly prefer to be coplanar and thus discourage coördination of an additional ligand which depends on its chelate nature for coördinating stability. These inferences concerning improbable or unfavorable configurations may prove useful in postulating structures for those substances which were found and studied in this investigation.

[Ni ophen$_3$][Ni(CN)$_4$]·4H$_2$O.—Both the infrared spectrum and the magnetic susceptibility of the rose-red, crystalline product can be interpreted satisfactorily on the basis of this formulation.

Infrared absorption frequencies have previously been determined for K_2[Ni(CN)$_4$]·H$_2$O[10] and for [Ni ophen$_3$] (ClO$_4$)$_2$.[11] The spectrum of the former consists of only a few absorption bands; that assigned to the C≡N stretching frequency is the most intense and occurs at 2128 cm.$^{-1}$. The latter compound exhibits a very complex absorption spectrum which, fortunately for the present consideration, does not include any appreciable absorption in the C≡N region. Considered together the spectra of [Ni ophen$_3$]$^{++}$ and [Ni(CN)$_4$]$^=$ simulate the spectrum obtained for the product in question; no significant shifts or otherwise noticeable changes are in evidence.

A compound with an empirical formula Ni ophen$_{1.5}$(CN)$_2$·2H$_2$O has been reported by Cambi, *et al.*,[9] to have a molar susceptibility of 1885 × 10^{-6} c.g.s. units at 21° corresponding to an effective magnetic moment of 2.20 Bohr magnetons per nickel(II) atom. Although no specific details of preparation were given, there appears to be little doubt that it is the same product described here, since our respective magnetic measurements and chemical analyses agree so well. In order to account for their results they proposed that the substance consists of a paramagnetic cation involving nickel with two unpaired electrons and a diamagnetic anion in which nickel has all its electrons paired. The magnetic and spectral data presented herein lend support to this contention.

Yellow Ni ophen(CN)$_2$(H$_2$O).—In order to isolate this substance in relatively pure form, it is necessary to conform closely to the procedural details set forth above for its preparation; otherwise the initial yellow product may in part undergo transformation to the lavender substance. Once the product is obtained in a dry state, it is resistant to such change; except for loss of water, no noticeable effect is produced by heating to 200°. When immersed in pure water at ordinary temperatures, the yellow solid changes in the course of several hours to the lavender form. The transformation thus appears to involve hydrolytic dissociation prior to rearrangement into the new form.

An unusual magnetic susceptibility is exhibited by the yellow complex, so unusual in fact that several attempts were made to isolate what might be inferred from magnetic measurements to be a purer product. As a general but somewhat fallible rule, complexes of nickel(II) which are yellow in color are found to be diamagnetic. It could therefore be suspected that the paramagnetism observed for the compound in question arises from contamination by nickel cyanide, the lavender compound, or both. Steps taken to minimize contamination by nickel cyanide proved to be adequate by chemical analysis. Visual and magnetic studies indicate that the rate of transformation of the yellow complex into the more paramagnetic lavender form, although appreciable at higher temperatures, is very slow at 0°. A batch of the yellow product after remaining in contact with its supernatant liquid for 20 hr. at 0° showed no evident change in color; its molar susceptibility on measurement was found to be + 1400 c.g.s. units. Thus by comparison, the magnetic susceptibility given in Table I for the yellow product isolated

---

(10) M. F. A. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

(11) A. A. Schilt and R. C. Taylor, *ibid.*, in press.

soon after preparation seems to be reliable in order of magnitude at least.

Infrared measurements reveal another unusual property of the yellow complex. Its absorption characteristics for the 2000–2500 cm.$^{-}$ region of the spectrum are shown in Fig. 1; absorption band frequencies observed for the entire region examined are listed in Table II. The most striking feature of the absorption spectrum is the presence of three closely grouped bands in the C≡N region. The two additional bands are not likely to be Raman lines which have become infrared active nor can they reasonably be assigned to vibrations in the 1,10-phenanthroline ligand.[11] It is surmised therefore that not all of the cyanide groups in the complex are equivalently bound to nickel(II). Recent evidence through X-ray analysis has established a dimeric structure of the hexacyanodinickelate(I) ion through bridged C≡N groups.[12] In order that the infrared analysis agrees with the X-ray results, El Sayed and Sheline[13] were required to propose a structure in which the Ni ions are bridged through two C≡N groups by way of 3 centered bonds. It appears that a similar condition may exist in the case of the yellow complex under consideration, although spectral data for the two are not completely analogous.

Because of the unusual properties noted above, it would be of considerable theoretical interest to ascertain the structure of the yellow complex. Unfortunately a crystalline product suitable for X-ray examination could not be prepared, furthermore no suitable solvent could be found for measurements of molecular weight, conductivity or dipole moment; so for the present a reliable elucidation of structure is not possible.

Lavender Ni ophen$(CN)_2(H_2O)_{0.5}$.—Both the infrared absorption and magnetic property of the lavender complex are indicative of unusual structural features.

The magnetic moment per nickel atom of 2.26 Bohr magnetons found for this substance might be interpreted in either of two ways. One possibility is that the nickel ions occur in two different modes of combination, one with octahedral symmetry with respect to ligand arrangement and the other with planar symmetry, such that one-half of the total nickel atoms retain two unpaired electrons. Another possibility is that the arrangement of ligands is not completely symmetrical and thus constitutes a tetragonal complex. In this event the magnetic moment for nickel(II) could conceivably lie somewhere between the theoretical limits 0–2.83 Bohr magnetons depending upon the symmetry of the ligand field. In regard to this consideration it is observed that temperature has a marked influence upon the color exhibited by the lavender complex. At liquid nitrogen temperatures the solid is pink-red, on warming its color turns to lavender and on heating it changes to violet and thence to a dull grey. These color changes are reversible and independent of hydration. Such behavior, in terms of the general theory of d-d spectra and the crystal or ligand field,[14] suggests a rather unsymmetrical arrangement of ligands and thus could be construed along with the magnetic data as being indicative of a tetragonal complex.

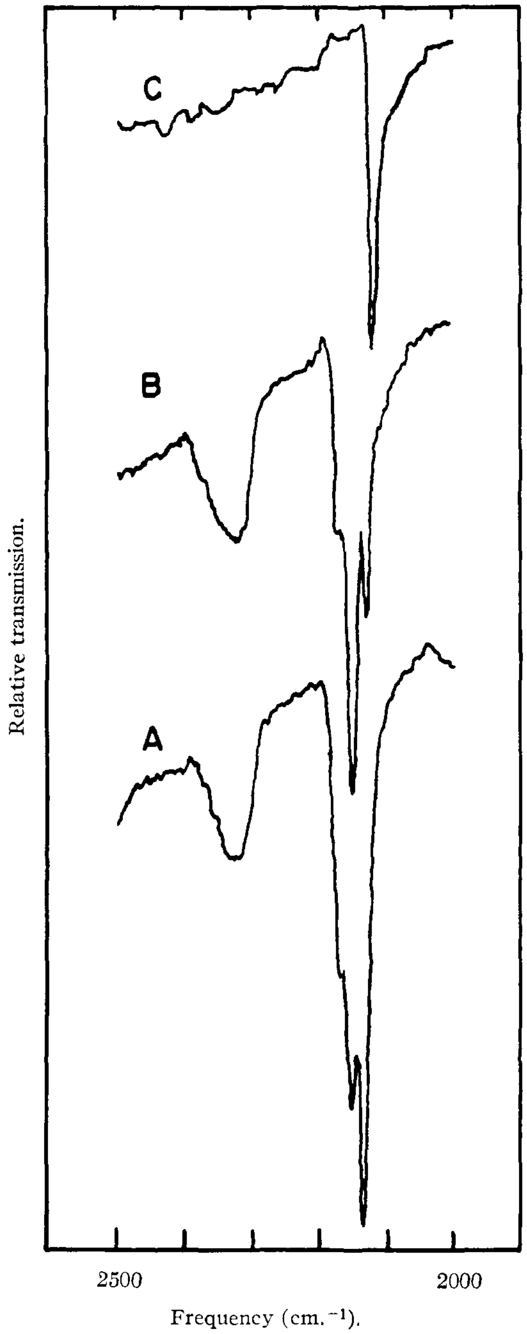

Fig. 1.—The infrared spectra of the nickel(II) complexes in the C≡N region: A, yellow Ni ophen$(CN)_2(H_2O)$; B, lavender Ni ophen$(CN_2)(H_2O)_{0.5}$; C, [Ni ophen$_3$] [Ni$(CN)_4$]. $4H_2O$. These curves have different base lines.

An interesting aspect of the infrared spectra shown in Fig. 1 is the pronounced change in relative intensities of the several bands in the C≡N region

---

(12) R. Nast and W. Pfab, *Naturwissenschaften*, **39**, 300 (1952).

(13) M. F. A. El-Sayed and R. K. Sheline, THIS JOURNAL, **78**, 702 (1956).

(14) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 368–372.

produced when the yellow complex is irreversibly transformed into the lavender complex. If the appearance of additional bands in this region is due to cyanide bridging, then it would follow that an increase in extent of bridging should be mirrored by changes in relative intensities. Whether or not such is the case here remains to be substantiated.

Additional studies which might reveal more about the structural features of the lavender complex were unfortunately precluded by failure to find a solvent which would dissolve sufficient amounts to enable measurement of molecular weight, dipole moment or conductivity.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Structure of the Reaction Product of Phenylacetylene with Iron Pentacarbonyl

BY J. R. LETO AND F. A. COTTON

RECEIVED SEPTEMBER 8, 1958

A compound first prepared by Jones, Wailes and Whiting in 1955 has been further studied. It is concluded from analytical data that its formula is $C_{20}H_{12}O_4Fe$ and not $C_{20}H_{10}O_4Fe$. Detailed study of the infrared spectrum and the fact that it has a dipole moment of ~3 Debye units lead to the proposal of a structure in which a diphenylcyclopentadienone is bonded by π electrons to an $Fe(CO)_3$ group.

Introduction

In 1955 Jones, Wailes and Whiting[1] reported the isolation of a compound with the formula $C_{20}H_{10\text{ or }12}O_4Fe$(I), their analytical accuracy being insufficient to distinguish between 10 or 12 hydrogen atoms. This compound was obtained in very small quantities by adding $Ni(CO)_4$ to a mixture of $Fe(CO)_5$ and phenylacetylene in aqueous ethanol and acetic acid. Without the $Ni(CO)_4$ no reaction occurred, but upon addition of $Ni(CO)_4$ the usual carbonylation reaction producing $C_6H_5C(COOC_2H_5)=CH_2$ proceeded essentially quantitatively and traces of I were found among the products. Jones, *et al.*, proposed that I is actually $C_{20}H_{10}O_4Fe$ with structure a, Fig. 1. Since, however, transition metal acetylides are commonly unstable, whereas I is extremely stable, we have considered that I might have the structure b (Fig. 1)[2] and thus be $C_{20}H_{12}O_4Fe$. With this in mind, we felt that the compound merited further study. We have confirmed its existence, preparing it by the same irrational procedure used by Jones, *et al.*, with slight modifications and have determined a number of its properties which bear on its constitution and structure. It appears to us that the evidence now available is inconsistent with structure a, but consistent with structure b.

Experimental

Preparation.—This was carried out in essentially the manner described by Jones, Wailes and Whiting.[1] The yield is increased somewhat (from 3.3 to 6.0%) by employing longer reaction times, and especially if the material is allowed to crystallize overnight from the cooled solution. In a typical run 2.2 g. of I was obtained from a reaction mixture consisting of 19.4 g. of $Fe(CO)_5$, 4.9 g. of $Ni(CO)_4$ and 25 g. of phenylacetylene, which had been held at 70° for 3 hr. Altogether a stock of 6.5 g. of I was accumulated from 4 runs. The product was purified as described by Jones, *et al.*, and had a melting point of 221–222° (222° reported[1]).

Purification by Chromatography.—A column of 200 g. of alumina was thoroughly washed with benzene and a solution of 0.2 g. of I in benzene was put on the column. Elution was carried out slowly by using a benzene–chloroform mixture, gradually increasing the proportion of chloroform. No separation of the band occurred. Elution was continued using benzene–acetone mixtures and again no separation was observable. Elution was then completed with pure acetone from which I was crystallized and found to have the same melting point as before.

Magnetic Susceptibility.—The bulk susceptibility was measured on the solid material using a Gouy balance. Material which was not rigorously purified shortly before measurement and carefully protected from light was found to be far less diamagnetic than would be expected and on some occasions slightly paramagnetic. The molar susceptibility obtained on the most highly purified and carefully handled sample was -40.0×10^{-6} c.g.s.μ which is still less than would be expected from Pascal's constants.

Nuclear Magnetic Resonance.—The proton resonance spectrum of a saturated solution of the iron compound in acetone-d_6 was taken in an effort to decide the number and kinds of protons in the molecule. The highest power level of a Varian 4300B high resolution spectrometer was used, and the spectrum was scanned at various speeds; only one weak resonance was observed at +1.68 p.p.m. from water and is without any doubt due to the phenyl protons. In our experience compounds containing acetylenic or olefinic protons have a resonance in the region +0.7 to +1.0 p.p.m. from water, but a careful search in this region (and all regions) yielded nothing. The phenyl resonance peak height (or area) in the saturated solution of the iron compound and the peak height (or area) of the cyclopentadienyl protons of ferrocene (added in mole for mole amount to the solution) were the same within experimental error—that is 10 protons per mole in ferrocene gave the same area under resonance peak as all the observable protons per mole (phenyl) in the iron compound. Although this indicates that the 2 other protons are not "masked" by the phenyl resonance, it does not positively disprove their existence. The observed peak is sufficiently weak that in our judgment another peak $^1/_5$ its intensity could escape detection.

Infrared Spectra.—Infrared spectra were taken on saturated solutions in CS_2, $CHCl_3$ and CCl_4 and on the solid mulled in Nujol and hexachlorobutadiene and pressed in KBr. Using 0.1 mm. cells, the solutions were all too dilute to reveal any but the strongest bands. The spectrum of pure liquid phenylacetylene was also run for comparison. All of the observed bands are listed in Table III. A Perkin–Elmer model 21 double beam spectrometer equipped with a rock-salt prism was used, employing both scanning cams to obtain the best possible resolution around 2000 cm.$^{-1}$.

Measurement of Dipole Moment.—The dipole moment of the iron compound in benzene solution was calculated in the usual way[3] from measurements of the total polarization and the electronic polarization of the molecule. The di-

---

[1] E. R. H. Jones, P. C. Wailes and M. C. Whiting, *J. Chem. Soc.*, 4021 (1955).

[2] We cannot tell from our experiments which isomer of diphenylcyclopentadienone is present and so we write structure b in a generic way. Our concern has been with the general structure and not with this detail.

[3] See, for example, R. J. W. LeFevre, "Dipole Moments," Methuen and Co., London, 1953.