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Contribution from the Department of Chemistry,
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Infrared Spectroscopic Study of Isonitrile Derivatives of the Iron Carbonyl Halides

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The complexes $Fe(CO)_{4-n}(CNR)_nX_2$, where $n = 0$–4, R = *p*-tolyl or *t*-butyl, and X = Cl, Br, or I, were prepared and the infrared spectra studied in the carbonyl and isonitrile stretching regions. The π-electron accepting abilities of the coordinated carbonyl and isonitrile groups are discussed. Structures of a number of these compounds are postulated on the basis of the number and intensity of the observed infrared bands. Spectral shifts in a series of compounds are found to correlate well with the electronegativities of the halogens.

Introduction

Continuing infrared spectroscopic study of derivatives of transition metal carbonyls, we have investigated the isonitrile derivatives of the iron tetracarbonyl dihalides. Although a number of derivatives of these carbonyl halides have been reported previously,[1-4] a systematic study of these compounds in the carbonyl stretching region has not been made. The replacement of carbonyl groups by isonitrile ligands enables us to study the N–C stretching frequencies in these derivatives. Thus we are able to study the π-electron accepting abilities of both ligands in this series of complexes.

Previous infrared studies[5-9] on mixed isonitrile–carbonyl complexes have indicated that the carbonyl group is a better π-electron acceptor than the isonitrile group. Hence, when both are present, the C–O group bears the greater burden of charge removal from the central metal atom. In carbonyl complexes in which the central metal atom is in a low valence state, for example, the group VI carbonyls, the buildup of negative charge on the metal atom can be relieved by π-electron donation from the metal to the empty π-antibonding orbitals on the carbon monoxide ligand. This lowers the bond order of the C–O bond, thereby lowering the C–O stretching frequency. As the charge on the metal atom is increased in the series Cr^0, Mn^+, Fe^{+2}, the amount of π-electron donation from metal to the carbonyl group decreases, thus increasing the C–O bond order and the resulting C–O stretching frequency.[10]

As shown by a study of Cotton and Zingales,[8] isonitrile molecules being formally isoelectronic with carbon monoxide may function both as σ-donors and π-electron acceptors. Their σ-donor ability is greater than that of carbon monoxide, and this ability is enhanced in complexes with metals in high oxidation states. The π-electron accepting ability of isonitrile ligands is exhibited to a degree in complexes with metals in low or negative oxidation states, but their ability to remove charge is always inferior to that of carbon monoxide. Our results confirm this hypothesis.

We were also able to correlate the inductive effect of the halogens due to their varying electronegativities with the observed infrared spectral shifts.

Experimental

Materials.—The iron tetracarbonyl dihalides were prepared according to the procedures of Hieber and Bader.[11] $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$ were purified by sublimation. $Fe(CO)_4Br_2$ sublimes readily at 40–45° (1–5 mm.) to give long reddish brown needles. $Fe(CO)_4I_2$ sublimes at 65–70° (5 mm.) to give long brownish black needles. $Fe(CO)_4Cl_2$ could not be sublimed without considerable decomposition. All three complexes were stored in darkened bottles, at −25°. Even at this temperature, $Fe(CO)_4Cl_2$ decomposes slowly.

t-Butyl and *p*-tolyl isonitriles were prepared according to the procedure of Ugi and Meyr.[12]

t-Butylisonitrileiron tetracarbonyl and di-(*t*-butylisonitrile)-iron tricarbonyl were prepared according to the procedures of Cotton and Parish.[7]

Although the *p*-tolylisonitrileiron tetracarbonyl and di-(*p*-tolylisonitrile)iron tricarbonyl complexes are new, they were prepared by a method similar to that of Hieber and von Pigenot.[13] This procedure is described below.

***p*-Tolylisonitrileiron Tetracarbonyl.**—A glass reaction tube 50 cm. long and 2 cm. in diameter equipped with a stopcock was flushed thoroughly with dry nitrogen. Iron pentacarbonyl (4 g., 0.02 mole) was pipetted into this tube. The reaction tube and its contents were cooled to −190°, evacuated, and flushed with nitrogen, this procedure being repeated twice. *p*-Tolylisonitrile

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(1) L. W. Hieber and A. Thalhofer, *Angew. Chem.*, **68**, 679 (1956).
(2) W. Hieber and D. von Pigenot, *Chem. Ber.*, **89**, 610 (1956).
(3) G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).
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(6) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
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(10) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).
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(12) I. Ugi and R. Meyr, *ibid.*, **93**, 239 (1960).
(13) W. Hieber and D. von Pigenot, *ibid.*, **89**, 193 (1956).

(2.4 g., ~0.02 mole) was then pipetted into the tube, and the mixture was cooled to −190°, evacuated, flushed with nitrogen, and then evacuated to 10^{-2} mm. pressure. The mixture then was heated at 65° for 4 hr., after which time the evolution of CO had ceased. The mixture was cooled to room temperature and pumped on for 48 hr. to remove any unreacted volatile materials. The dark residue was sublimed at 75° (10^{-3} mm.), maintaining the cold finger at −30°. A large quantity of $Fe(CO)_4[CNC_7H_7]$ in the form of pale yellow crystals was removed.

Di-(*p*-tolylisonitrile)iron Tricarbonyl.—This complex was prepared in a similar manner. A typical preparation involved the reaction of 2.0 g. (0.01 mole) of iron pentacarbonyl with 2.5 g. (~0.02 mole) of *p*-tolylisonitrile. Reaction was complete in 5 hr. at 80–90°. Sublimation of the dark solid at 90° (10^{-3} mm.) removed volatile products including *p*-tolylisonitrileiron tetracarbonyl. After all the monosubstituted product was removed (based on infrared data), the disubstituted derivative was obtained by recrystallization from light petroleum ether (30–60°) in the form of pale yellow crystals.

All the mixed isonitrile carbonyl iron dihalide complexes reported here are new. They were prepared by methods analogous to those described by Hieber and von Pigenot.[2] Anhydrous solvents were employed and a nitrogen atmosphere was maintained throughout all preparations.

$Fe(CO)_3(CNR)X_2$. Method 1.—$Fe(CO)_4(CNR)$ (1 mmole) was dissolved in 10 ml. of ether and this mixture was placed in a two-necked flask equipped with nitrogen bleed, dropping funnel, and $CaCl_2$ drying tube. X_2 (1 mmole, except Cl_2, in which case a saturated ether solution was employed), in 10 ml. of ether was added dropwise. An excess of halogen must be avoided since oxidation occurs readily, especially in the case of chlorine addition. The reaction mixture was reduced to half-volume by the nitrogen stream and the product precipitated out. It was collected by filtration and washed with three 5-ml. portions of cold (−20°) ether.

Method 2.—$Fe(CO)_4X_2$ (1 mmole) was dissolved in a minimum of ether (~100–120 ml.) and filtered. This was placed in the previously described reaction flask and to this solution a solution of 1 mmole of CNR in 10 ml. of ether was added dropwise. After the volume of the solution had been reduced to ~10–15 ml. by the nitrogen stream, the product was filtered off and washed with ether as before.

The chloride and bromide complexes were prepared according to method 1 and the iodide complexes were prepared by both methods. Based on the infrared data, the two iodide complexes were identical.

$Fe(CO)_2(CNR)_2X_2$.—The disubstituted derivatives were prepared by method 1 starting with $Fe(CO)_3(CNR)_2$. The iodide complex was also prepared by method 2 using 2 mmoles of the isonitrile. Again, they were identical.

$Fe(CO)(CNR)_3X_2$.—The trisubstituted derivatives were prepared by method 2 with the revision that the $Fe(CO)_4X_2$ ether solution was added dropwise to the ether solution containing 3 mmoles of CNR. The *t*-butyl complexes could not be prepared. This result is in line with the observation of Hieber and von Pigenot.[13] The iodide complex was also prepared by adding a solution of 1 mmole of $Fe(CO)_4I_2$ in 15 ml. of tetrahydrofuran to a refluxing solution of 3 mmoles of *p*-tolylisonitrile in 15 ml. of ether. The total time of reflux was 1 hr. Removal of solvent with nitrogen gave the reddish brown product which was washed thoroughly with cold ether.

***cis*-$Fe(CNR)_4X_2$.**—These complexes were prepared according to the procedure of Malatesta, Sacco, and Padoa,[14] using ethyl alcohol as the solvent. The tetra-*t*-butylisonitrile derivatives are new. All complexes decompose slowly upon extended exposure to air and light, the stability decreasing in the order I > Br > Cl. Storage is possible in darkened bottles.

Infrared Measurements.—All infrared spectra were recorded on a Perkin-Elmer Model 421 grating spectrophotometer equipped with a dual grating interchange. The scanning rate, peak position determination, and wave number calibration were reported in a previous paper.[5] Frequencies are believed accurate to ±0.5 cm.$^{-1}$ for carbonyl bands and ±1.0 cm.$^{-1}$ for the isonitrile bands.

All complexes were run in chloroform solution in 1-mm. NaCl liquid cells.

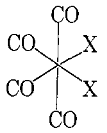
Analysis.—Due to their instability, good analyses could not be obtained for all the compounds. However, all were characterized by their infrared spectra and melting or decomposition points. See Table I for analysis data.

Results

The carbonyl and isonitrile frequencies of the complexes prepared and studied in this work are given in Table II.

Discussion

$Fe(CO)_4X_2$ and $Fe(CNR)_4X_2$.—Various workers have shown by infrared studies[15–17] and by dipole moment measurements[18] that the irontetracarbonyl dihalides exist in the *cis* configuration (I). The corresponding iron tetraisonitrile dihalides exist in two forms, α and β.[14] The α form corresponds to the *cis* isomer and is quite soluble in organic solvents. The tetraisonitrileiron dihalide complexes prepared in this study, on the basis of the infrared data, appear to be the *cis* isomers.



I

The *cis* forms of $Fe(CO)_4X_2$ and $Fe(CNR)_4X_2$ have C_{2v} and pseudo C_{2v} symmetry, respectively, neglecting in the latter case any asymmetry due to the nonlinearity of the C–N–R groups. These complexes should have four infrared-active carbonyl and isonitrile stretching frequencies corresponding to the $A_1^{(1)}$, $A_1^{(2)}$, B_1, and B_2 normal modes of vibration.[19]

According to Orgel[10] and Cotton and Kraihanzel,[6] for molecules of the type *cis*-$[L_2M(CO)_4]$, the *trans* pair of carbonyl groups gives rise to a weak $A_1^{(1)}$ mode and an antisymmetric B_1 stretching mode. The other two carbonyls give rise to an $A_1^{(2)}$ (symmetric) mode and a B_2 (antisymmetric) mode of comparable intensity. The two A_1 modes interact; the weak $A_1^{(1)}$ mode of the *trans* carbonyl borrows intensity from the *cis* $A_1^{(2)}$ mode. Thus for *cis*-$[L_2M(CO)_4]$, where M is a d^6 atom or ion (Cr^0, Mn^+, Fe^{+2}), we expect a pair of bands, one very strong, the other weak, separated by 40–120 cm.$^{-1}$ (depending on the oxidation state of the central metal atom), and two additional bands of intermediate strength. We have cited in Table III from our results and results available in the literature the dependence on the oxidation state of the central metal atom of the weak band–strong band separation.

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[14] L. Malatesta, A. Sacco, and G. Padoa, *Ann. Chim.* (Rome), **43**, 617 (1953); *Chem. Abstr.*, **48**, 7476*i* (1954).

[15] K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

[16] C. C. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2582 (1961).

[17] M. A. Bennett and R. J. H. Clark, *Chem. Ind.* (London), 861 (1963).

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[19] Superscript (1) of A modes refers to *trans* CO, (2) refers to *cis*.

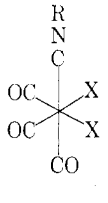
TABLE I

Compound[a]	Color	M.p. or dec. pt., °C.	Analysis Calcd. C	Calcd. H	Found C	Found H
$Fe(CO)_3(CNR)Cl_2$	Yellow	90–92 dec.	40.30	2.15	35.89	3.28
$Fe(CO)_3(CNR')Cl_2$	Yellow		32.65	3.09		
$Fe(CO)_2(CNR)_2Cl_2$	Yellow-brown	~95 dec.	51.80	3.38	56.52	4.62
$Fe(CO)_2(CNR')_2Cl_2$	Yellow	180–185 dec.	41.30	5.20	39.68	5.83
$Fe(CO)(CNR)_3Cl_2$	Yellow	95–100 dec.	59.40	4.18	53.74	3.91
$Fe(CNR)_4Cl_2$	Blue (*trans*) Yellow-brown (*cis*)	~130 dec.	64.55	4.74	63.88	4.75
$Fe(CNR')_4Cl_2$	Yellow (*cis*)	181–184	52.00	7.90		
$Fe(CO)_3(CNR)Br_2$	Reddish brown	92–95 dec.	31.70	1.70	33.86	3.19
$Fe(CO)_3(CNR')Br_2$	Reddish orange	90–95 dec.	25.05	2.35	25.23	2.56
$Fe(CO)_2(CNR)_2Br_2$	Dark brown	90–95 dec.	42.60	2.79	47.31	3.69
$Fe(CO)_2(CNR')_2Br_2$	Yellow-brown	95–98 dec.	32.90	4.14	31.69	4.13
$Fe(CO)(CNR)_3Br_2$	Yellow-orange	~175 dec.	50.50	3.56	50.63[b]	3.79
$Fe(CNR)_4Br_2$	Gray-brown	~200 dec.	56.20	4.11	53.54	4.07
$Fe(CNR')_4Br_2$	Reddish brown	151–155	43.75	6.52	38.70	5.64
$Fe(CO)_3(CNR)I_2$	Brown-black	98–100 dec.	25.90	1.38	27.13	1.57
$Fe(CO)_3(CNR')I_2$	Light brown	70–74 dec.	20.15	1.90	18.98	1.98
$Fe(CO)_2(CNR)_2I_2$	Reddish brown	113–115 dec.	36.03	2.35	35.35	2.54
$Fe(CO)_2(CNR')_2I_2$	Light brown	108–111 dec.	27.10	3.42	27.37	3.51
$Fe(CO)(CNR)_3I_2$	Reddish brown	80–85 dec.	43.50	3.08	54.18	4.08
$Fe(CNR)_4I_2$	Dark brown	198–201	49.35	3.63	48.43	3.58
$Fe(CNR')_4I_2$	Dark brown	111–115	37.40	5.66	40.37	6.22
$Fe(CO)_4(CNR)$	Light yellow	50–52	50.55	2.48	50.31	2.46
$Fe(CO)_4(CNR')$[c]	Yellow	48–49	43.10	3.60	44.03	4.12
$Fe(CO)_3(CNR)_2$	Yellow	101–103	61.00	3.78	60.79	3.91
$Fe(CO)_3(CNR')_2$[d]	Bright yellow	92–93	51.10	5.90	49.66	5.79

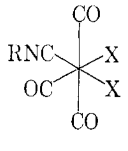
[a] R = *p*-tolyl, R′ = *t*-butyl. [b] Average of two separate analyses. [c] Reference 7, m.p. 53.5–54.5°. [d] Reference 7, m.p. 98–98.5°.

The infrared data for the $Fe(CNR)_4X_2$ complexes support the conclusions drawn for the analogous carbonyl complexes. Although the symmetry is probably something less than C_{2v} due to the fact that the C–N–R group is not linear,[7,8] the weak band–strong band separation is quite pronounced. The separation is less than in corresponding carbonyls. This result is expected since it previously has been shown[5] that the isonitrile ligand is not as sensitive as the carbonyl groups to changes in electron density.

$Fe(CO)_3(CNR)X_2$.—Both possible complexes have pseudo-C_s symmetry, II and III. For II we expect three carbonyl stretching frequencies: an A′ mode due to the unique carbonyl group and an A′ mode and an A″ mode due to the equatorial carbonyls. Furthermore, the A′ modes interact. The unique A′ mode should be quite strong and the equatorial A′ and A″ modes of approximately equal intensity. This result is in contrast to the infrared spectrum of III, for which we expect a very weak A′ mode (axial CO), a strong A″ mode (axial CO), and a very strong A′ mode (equatorial CO). The infrared data (see table II) support structure II. The isonitrile group gives rise to an A′ mode in either II or III.



II



III

Although it has been shown that the four carbonyls in $Fe(CO)_4X_2$ are equivalent with respect to carbon monoxide exchange,[20] the observed carbonyl stretching frequencies and their relative intensities suggest that the substitution of the isonitrile occurs *cis* to the halogen instead of *trans*. The result would be consistent with the data for monosubstitution in $Mn(CO)_5X$[20,21] and with disubstitution of tertiary phosphines in $Fe(CO)_4X_2$.[3]

Similarly, as with $Fe(CO)_4X_2$, the carbonyl stretching frequencies lie highest for the chloride and lowest for the iodide. This result is to be expected. The more highly electronegative chlorine is a better remover of charge from the central metal atom than is the iodine, hence the amount of back donation of charge from the central metal atom into the antibonding π-orbitals on the carbonyl group is less in the chloride than it is in the iodide complexes. The resulting C–O bond order, therefore, is greatest in the chloride complexes, giving rise to a higher stretching frequency. This same argument also applies to the isonitrile frequencies, the C–N stretching frequency being greatest for the chloride complexes.

Orgel[10] and Cotton and Kraihanzel[6] have suggested that the stretching frequency of a carbonyl group *trans* to an L group in substituted octahedral metal carbonyls is lowered to a greater extent than is the stretching frequency of a carbonyl group *cis* to L. From the data in Table II we show in Table IV the lowering of the C–O frequency of the carbonyl *trans* and *cis* to the isonitrile.

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(20) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

(21) H. B. Gray, E. Billig, A. Wojcicki, and M. Farona, *Can. J. Chem.*, **41**, 1281 (1963).

TABLE II

INFRARED DATA[a]

Compound	ν_{NC}	ν_{CO}
$Fe(CO)_4Cl_2$		(A_1^1) 2166.9 (w), (A_1^2,B_1) 2125.8 (vs), (B_2) 2081.7 (s)
$Fe(CO)_4Br_2$		(A_1^1) 2155.0 (w), (A_1^2) 2112.4 (s), (B_1) 2108.6 (s), (B_2) 2081.6 (s)
$Fe(CO)_4I_2$		(A_1^1) 2134.7 (w), (A_1^2,B_1) 2089.4 (vs), (B_2) 2068.4 (s)
$Fe(CO)_3(CNR)Cl_2$	(A') 2215.9 (vs)	(A') 2132.5 (s), (A') 2096.5 (m), (A'') 2070.7 (m)
$Fe(CO)_3(CNR')Cl_2$	(A') 2227.3 (vs)	(A') 2131.0 (s), (A') 2093.1 (m), (A'') 2068.2 (m)
$Fe(CO)_3(CNR)Br_2$	(A') 2209.6 (vs)	(A') 2120.8 (s), (A') 2088.0 (m), (A'') 2063.4 (m)
$Fe(CO)_3(CNR')Br_2$	(A') 2222.9 (vs)	(A') 2120.1 (s), (A') 2084.8 (m), (A'') 2059.8 (m)
$Fe(CO)_3(CNR)I_2$	(A') 2197.1 (vs)	(A') 2103.0 (s), (A') 2071.4 (m), (A'') 2049.4 (m)
$Fe(CO)_3(CNR')I_2$	(A') 2208.2 (vs)	(A') 2101.6 (s), (A') 2068.2 (m), (A'') 2047.5 (m)
$Fe(CO)_2(CNR)_2Cl_2$	(B_1) 2194.4 (vs), (A_1) 2162.5 (m)	(A_1) 2086.8 (m), (B_2) 2047.8 (m)
$Fe(CO)_2(CNR')_2Cl_2$	(B_1) 2207.1 (vs)	(A_1) 2082.1 (m), (B_2) 2039.8 (m)
$Fe(CO)_2(CNR)_2Br_2$	(B_1) 2185.3 (s), (A_1) 2170.5 (m, sh)	(A_1) 2080.0 (m), (B_2) 2042.5 (m)
$Fe(CO)_2(CNR')_2Br_2$	(B_1) 2198.6 (vs)	(A_1) 2075.4 (m), (B_2) 2035.2 (m)
$Fe(CO)_2(CNR)_2I_2$	(A_1) 2188.4 (m), (B_1) 2166.8 (s)	(A_1) 2073.7 (m), (B_2) 2039.2 (m)
$Fe(CO)_2(CNR')_2I_2$	(A_1) 2201.8 (m), (B_1) 2179.7 (vs)	(A_1) 2068.9 (m), (B_2) 2030.9 (m)
$Fe(CO)(CNR)_3Cl_2$	(A') 2188.0 (sh), (A'') 2173.7 (vs), (A') 2166.8 (vs)	(A') 2037.6 (m)
$Fe(CO)(CNR)_3Br_2$	(A') 2185.0 (w, sh), (A'') 2170.3 (vs), (A') 2143.3 (vs)	(A') 2035.4 (m)
$Fe(CO)(CNR)_3I_2$	(A') 2180.0 (sh), (A') 2166.2 (vs), (A') 2140.8 (vs)	(A') 2031.7 (m)
$Fe(CNR)_4Cl_2$	(A_1^1) 2195.0 (w), (A_1^2) 2159.6 (s), (B_1) 2152.0 (s), (B_2) 2131.2 (m)	
$Fe(CNR')_4Cl_2$	(A_1^1) 2207.2 (m), (A_1^2,B_1) 2170.4 (vs), (B_2) 2154.0 (s)	
$Fe(CNR)_4Br_2$	(A_1^1) 2189.7 (w), (A_1^2) 2152.2 (vs), (B_1) 2142.2 (s), (B_2) 2131.6 (m)	
$Fe(CNR')_4Br_2$	2172.0 (vs)[b]	
$Fe(CNR)_4I_2$	(A_1^1) 2178.4 (m), 2130.1 (vs)[c]	
$Fe(CNR')_4I_2$	(A_1^1) 2198.1 (vw), 2163.1 (vs)[c]	

[a] Values given in wave numbers, symmetry of vibration and relative intensity given in parentheses; s, strong; v, very; m, moderate; w, weak; sh, shoulder. [b] This band is very broad and probably contains a number of C–N bands. [c] The extreme breadth of this low frequency band suggests that it contains the A_1^2, B_1, and B_2 normal modes.

TABLE III

Compound	ν_{CO}, cm.$^{-1}$	Weak band–strong band sepn., cm.$^{-1}$
cis-$[(P(C_2H_5)_3)_2Mo(CO)_4]$[10,b]	2012 ($A_1^{(1)}$) (w), 1907 ($A_1^{(2)}$)[a] (sh), 1895 (B_1) (vs), 1866 (B_2) (s)	117
$CF_3Mn(CO)_5$[10,c]	2144 ($A_1^{(1)}$) (w), 2050 (E) (s), 2025 ($A_1^{(2)}$) (s)	94
$Mn(CO)_5I$[10,d]	2136 ($A_1^{(1)}$) (w), 2056 (E) (s), 2017 ($A_1^{(2)}$) (s)	80
$Fe(CO)_4I_2$	2134.7 ($A_1^{(1)}$) (w), 2089.4 ($A_1^{(2)}$,B_1) (vs), 2068.4 (B_2) (s)	45.3
$Fe(CO)_4Br_2$	2155.0 ($A_1^{(1)}$) (w), 2112.4 ($A_1^{(2)}$) (s), 2108.6 (B_1) (s), 2081.6 (B_2) (s)	46.4
$Fe(CO)_4Cl_2$	2166.9 ($A_1^{(1)}$) (w), 2125.8 ($A_1^{(2)}$,B_1) (vs), 2081.7 (B_2) (s)	41.1

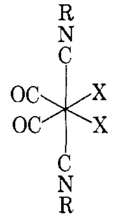
[a] Orgel[10] errs in calling this a B_1 mode. [b] R. Poilblanc and M. Bigorgne, *Compt. rend.*, **250**, 1064 (1960). [c] W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961). [d] E. W. Abel, M. A. Bennett, and G. Wilkinson, *Chem. Ind.* (London), 442 (1960).

The isonitrile lowers the stretching frequency of the carbonyl *cis* to it by ~20–30 cm.$^{-1}$, depending on the halogen, whereas the lowering of the *trans* carbonyl is of the order of 30–35 cm.$^{-1}$. This is consistent with data of Bigorgne as cited by Orgel.[9,10]

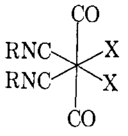
TABLE IV

		trans		*cis*	
		$A_1^{(1)}[Fe(CO)_4X_2]$ – $A'[Fe(CO)_3X_2(CNR)]$		$A_1^{(2)}[Fe(CO)_4X_2]$ – $A'[Fe(CO)_3X_2(CNR)]$	
X	R	cm.$^{-1}$	%	cm.$^{-1}$	%
Cl	*p*-Tolyl	34.4	1.69	29.3	1.40
	t-Butyl	35.9	1.77	32.7	1.56
Br	*p*-Tolyl	34.2	1.61	24.4	1.17
	t-Butyl	34.9	1.65	27.6	1.32
I	*p*-Tolyl	31.7	1.46	18.0	0.87
	t-Butyl	33.1	1.57	21.2	1.02

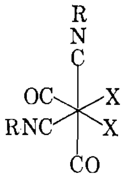
$Fe(CO)_2(CNR)_2X_2$.—These complexes may have either pseudo-C_{2v} symmetry (IV and V) or C_1 symmetry (VI). V has been ruled out on the basis of the infrared data and the results of Booth and Chatt.[3] For IV, we expect two carbonyl bands A_1 and B_2 of approximately equal intensity, one strong isonitrile band B_1, and a weak A_1 isonitrile band. We expect two carbonyl and two isonitrile bands for VI. Booth and Chatt prefer structure IV.



IV



V



VI

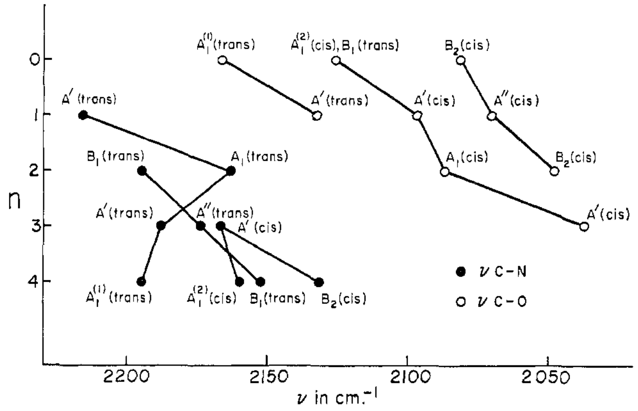
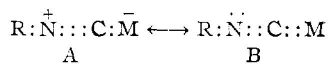


Fig. 1.—Correlation diagram for the CN and CO bands of the molecules $Fe(CO)_{4-n}(CNC_7H_7)_nCl_2$.

The observed spectra consist of two carbonyl bands of approximately equal intensity and two isonitrile bands of varying intensities (except for the chloride and bromide *t*-butyl isonitrile complexes where only one strong isonitrile band is observed, as is predicted for the B_1 mode of IV). The most intense isonitrile bands in all six of the disubstituted complexes follow the expected trend of decreasing frequency in the series chloride, bromide, iodide. The electronegative chlorine removes more charge from the metal atom, thereby increasing the donor ability of the isonitrile groups. The contribution of resonance form A is enhanced thereby raising the observed N–C stretching frequency.



$$\underset{A}{R{:}\overset{+}{N}{:}{:}{:}C{:}\overset{-}{M}} \longleftrightarrow \underset{B}{R{:}\overset{\cdot\cdot}{N}{:}{:}C{:}{:}M}$$

The appearance, in the *t*-butyl iodide complex, of a weaker band on the high-frequency side of the B_1 mode may perhaps be due to the weak A_1 mode which has gained intensity due to the nonlinearity of the C–N–R grouping. This nonlinearity may occur for one of two reasons: (1) The smaller inductive effect of the iodine as compared to the chlorine, *i.e.*, there is a greater contribution of resonance form B in the iodide complex. This will give rise to a significant bending of the C–N–C–$(CH_3)_3$ grouping. (2) The large iodide, by steric effect, may repulse the bulky $C(CH_3)_3$ groups to a greater extent than will the smaller chloride and bromide.

The appearance of two isonitrile bands in the *p*-tolyl complexes may also be explained by the preceding argument. The appearance of the additional bands in the chloride and bromide *p*-tolyl complexes as contrasted with the analogous *t*-butyl complexes may be explained as resulting from a greater contribution of resonance form B in the coordinated *p*-tolylisonitrile complexes. Previous work[5,8] has indicated that aryl isonitriles are better π-acceptors than alkyl isonitriles. In addition, the bulkier *p*-tolyl group may be more sterically affected by the halogen than the *t*-butyl group.

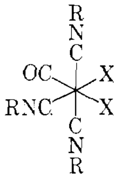
The slight asymmetry on the low-frequency side of the B_1 isonitrile bands in the chloride and bromide *t*-butylisonitrile complexes lends further support to the presence of a weak A_1 mode, hidden by the intense B_1 vibration.

The possibility of contamination by the presence of trisubstituted complex appears unlikely in view of the method of preparation of $Fe(CO)_2(CNR)_2X_2$.

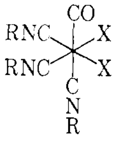
Although the possibility of VI has not been ruled out, our infrared data and the data of Booth and Chatt[3] both support IV.

The replacement of two carbonyls by isonitrile ligands increases the amount of back donation into the π-antibonding orbitals of the carbonyl. Therefore the stretching frequencies of the carbonyls are lowered. The relative decrease is not as great as it was in the monosubstituted complexes. Orgel found the same result.[10] The isonitrile stretching frequencies of the disubstituted complexes occur at lower frequencies than in the monosubstituted complexes because of the increased importance of resonance form B.

$Fe(CO)(CNR)_3X_2$.—If we proceed with the substitution of CNR for CO, using IV, we obtain VII. This molecule, of pseudo-C_s symmetry, should have a strong A′ mode due to the lone carbonyl. The three isonitrile groups give rise to a weak A′ mode and an intense A″ mode due to the *trans* pair of isonitriles and, finally, a band of moderate intensity due to the unique isonitrile. Although the infrared spectra are consistent with this model (see Table I), the data do not rule out possibility VIII.



VII



VIII

The amount of back donation of charge to the carbonyl group reaches a maximum in these complexes, hence the C–O stretching frequencies occur at very low values. The difference in going from chloride to iodide is very slight, 5.9 cm.$^{-1}$, indicating that the amount of back donation to the carbonyl is approximately the same in both cases.

The isonitrile frequencies continue to decrease as expected. The removal of C–O groups places the burden of charge removal on the isonitrile linkage.

Electronegativity.—Since the geometries of the halide complexes are identical in the series chloride, bromide, iodide, the observed infrared spectra should be a function of the properties of the halogen atom in these molecules. Various authors[20–24] have explained the reactivity of $Mn(CO)_5X$ on the basis of the polarizability or electronegativity of the halogen. Therefore, it is not surprising that plots of carbonyl or isonitrile frequencies of the same normal mode *vs.* the electro-

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(22) R. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).
(23) W. Hieber and K. Wollmann, *Chem. Ber.*, **95**, 1552 (1962).
(24) R. J. Angelici and F. Basolo, *Inorg. Chem.*, **2**, 728 (1963).
(25) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 93.

negativities of the halogens[25] present give linear relationships.

In Fig. 1 is shown a typical correlation diagram for the CO and NC bands in the series of compounds $Fe(CO)_{4-n}(CNC_7H_7)_nCl_2$.

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The Preparation and Properties of Some Complexes of the Type β-Diketonatobis(ethylenediamine)cobalt(III) Iodide and Bis(β-diketonato)tetrakis(ethylenediamine)dicobalt(III) Iodide

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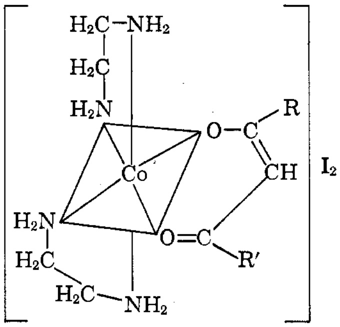
Seven mononuclear complexes of the general type β-diketonatobis(ethylenediamine)cobalt(III) iodide and four dinuclear complexes of the general type bis(β-diketonato)tetrakis(ethylenediamine)dicobalt(III) iodide have been prepared. The infrared spectra and ultraviolet and visible electronic spectra of these complexes have been measured and are found to support the structures proposed. The unique structure of one of the dinuclear complexes is briefly noted.

Introduction

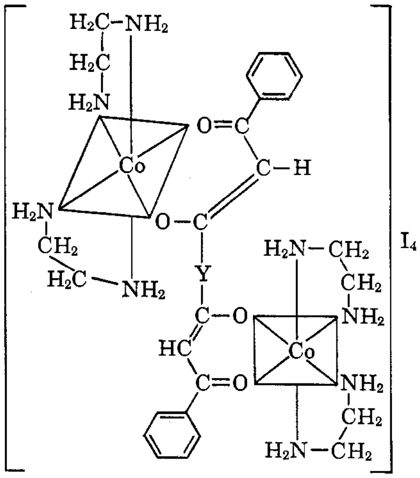
Werner[1] prepared and characterized a large number of dinuclear cobalt complexes which, in addition to stereochemical considerations, have many interesting properties, *i.e.*, intense color and large molecular rotations. These complexes have not been investigated extensively, mainly because they are extremely difficult to prepare. However, current work in coordination polymers has revived interest in the formation of polynuclear complexes. Coordination polymers are generally intractable, and very little information, other than composition and thermal stability, has been derived from them. A logical approach to the study of the preparation and properties of polymeric complexes consists in the preparation of monomeric, dimeric, and higher units and a comparison of their properties. An investigation of this kind perhaps would provide a greater insight into the formation and properties of the dinuclear complexes reported by Werner.

One method of preparing polymeric complexes involves the use of bisdifunctional ligands. Since the preparation and chelating properties of bis-β-diketones are well known, they were chosen as ligands in the study reported here. An additional advantage is that the corresponding β-diketones can be used to prepare the mononuclear complexes.

Werner reported the preparation of the β-diketonatobis(ethylenediamine)cobalt (III) cation in which the β-diketone was acetylacetone or propionylacetone.[2] The procedure which he outlined is not general for other β-diketones or bis-β-diketones, but by simple modifications we have prepared the complexes I–VII.[3] Similar procedures were used to prepare the dinuclear complexes VIII–XI.



I, R = R′ = CH_3
II, R = CH_3; R′ = C_2H_5
III, R = CH_3; R′ = CF_3
IV, R = CH_3; R′ = OC_2H_5
V, R = C_6H_5; R′ = OC_2H_5
VI, R = CH_3; R′ = C_6H_5
VII, R = R′ = C_6H_5



VIII, Y = nothing (chelate rings directly connected)
IX, Y = $-(CH_2)_2-$
X, Y = $-(CH_2)_8-$
XI, Y = p-C_6H_4-

Experimental

Ligands.—The following ligands were obtained commercially and used without further purification: 2,4-pentanedione (acetylacetone); 1-phenyl-1,3-butanedione (benzoylacetone); 1,3-diphenyl-1,3-propanedione (dibenzoylmethane); 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone); 1-ethoxy-1,3-butanedione (ethyl acetoacetate); 1-ethoxy-3-phenyl-1,3-propanedione (ethyl benzoylacetate).

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[1] A. Werner, *Ann.*, **375**, 1 (1910).

[2] A. Werner, J. E. Schwyzer, and W. Karrer, *Helv. Chim. Acta*, **4**, 113 (1921).

[3] Recently the complex with R = R′ = CF_3 has been reported: D. A. Buckingham and J. P. Collman, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, p. 36N.