290. *The Stereochemistry of Five-co-ordinate Compounds. Part I. Infrared Spectra of Some Iron*(0) *Compounds.*

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The infrared spectra of some compounds of the type $LFe(CO)_4$ and $L_2Fe(CO)_3$ ($L = Ph_3P$, Me·NC, Et·NC, Ph·NC, Bu^t·NC) and of $[(Ph{\cdot}NC)_5Co]^{1+}$ are reported and it is concluded from comparison with selection rules that the configurations are very probably trigonal bipyramidal. The preparation of the new Bu^t·NC compounds is described. An explanation is proposed for the fact that formation of a complex raises the NC frequency in Bu^t·NC, whereas there is a lowering in the analogous $(Me)_3Si{\cdot}NC$ and $(Me)_3Ge{\cdot}NC$ complexes made by Seyferth and Kahlen.

FIVE-CO-ORDINATE complexes are formed by each of the isoelectronic species Mn(-I), Fe(0), Co(I), and Ni(II), and their stereochemistry is of considerable interest. For those in which all five ligands are identical it has generally been supposed that the configuration would be either a trigonal bipyramid (TBP) or a rectangular pyramid (RP). The only other regular configurations, *viz.*, the plane pentagon and the pentagonal pyramid, have never been considered likely, nor will they be considered further here. The only known compounds with five identical ligands are $Mn(CO)_5^{1-}$, $Fe(CO)_5$, and several cations $[Co(CNR)_5]^{1+}$, where R = Me, Ph, or one of several *para*-substituted phenyls.

There is some infrared evidence to suggest that $Mn(CO)_5^{1-}$ and $HMn(CO)_5$ (in which the H atom probably has little if any steric effect) have TBP configurations.[1,2] Hieber

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[1] Wilson, *Z. Naturforsch.*, 1958, **13**b, 349.
[2] Cotton, Down, and Wilkinson, *J.*, 1959, 833.

and Wagner[3] believe that the close parallels between the physical properties of $HMn(CO)_5$ and $Fe(CO)_5$ indicate that the molecules are isosteric and hence very probably isostructural. There has been considerable controversy about the configuration of iron pentacarbonyl in the past few decades and even today its structure is not known with certainty. Ewens and Lister's[4] electron-diffraction studies certainly seemed to narrow the possible configurations to two, namely, the TBP and the RP. Although these authors chose the TBP model, inspection of their published diffraction curves indicates that the choice is far from being indisputable. Since that time various attempts have been made to provide conclusive evidence for one or the other of these configurations. Three independent measurements of the dipole moment have been reported,[5,6,7] and there is no doubt that when the total molar polarization is corrected for the electronic polarization, estimated from the refractive index for visible light, an apparent moment of ~0·60 is calculated. Weiss[7] suggests that this is due to failure to correct for atomic polarization and thus feels that the dipole-moment data are consistent with the trigonal bipyramid configuration. However, O'Dwyer[8] has maintained that, since the atomic polarization in nickel carbonyl is only ~10% of the electronic polarization whereas for $Fe(CO)_5$ it must be assumed to be ~20% in order to dispose of the apparent moment of ~0·60, it is not certain that Weiss is justified in his argument and conclusion. An unsuccessful attempt has been made[9] to determine the structure from the ^{13}C nuclear resonance spectrum.

Several studies of the vibrational spectrum of $Fe(CO)_5$ have been reported. Sheline and Pitzer,[10] from very limited data, favoured the TBP model. King and Lippincott[11] made a more detailed study of the infrared spectrum and also obtained a very limited amount of Raman data; they, too, favoured a TBP structure. Rather recently, O'Dwyer[8] has reported a reinvestigation of the infrared spectrum and has claimed that his data can be satisfactorily assigned to an RP model but not to a TBP model. However, these conclusions seem to depend critically on the genuineness of several bands reported by him, but not observed by others.[9]

The most conclusive spectral evidence to date does seem strongly to favour the TBP model. Stammreich *et al.*[12] recorded a very extensive Raman spectrum, which, together with an unusually complete set of infrared data,[9,13] can be satisfactorily assigned to the TBP model but not to the RP model.

So far as we are aware, there has been no published evidence as to the configurations of the $[Co(CNR)_5]^{1+}$ ions.

For five-co-ordinate complexes of the various atoms and ions mentioned above, in which there are two or more kinds of ligand, few experimental data indicative of configuration have been reported. While this work was in progress, Vohler[14] reported that the infrared spectrum of $[(Ph_3P)_2Co(CO)_3]^{1+}$ indicated D_{3h} symmetry for that ion. In this paper we describe the results of experimental study of the infrared spectra of some compounds of the type $LFe(CO)_4$ and $L_2Fe(CO)_3$, in the CO stretching region, where L is triphenylphosphine, and in both CN and CO stretching regions where L is an isocyanide. The CN stretching frequencies of $[(Ph\cdot NC)_5Co]^+$ are also reported.

The selection rules for CO stretching modes in all possible mono- and di-substituted molecules of the types $(RNC)M(CO)_4$ and $(RNC)_2M(CO)_3$, assuming substitution of RNC for CO in $M(CO)_5$ with preservation of initial configurations of both TBP and RP, have

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[3] Hieber and Wagner, *Z. Naturforsch.*, 1958, **13**b, 339.
[4] Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681.
[5] Bergman and Engel, *Z. phys. Chem.*, 1931, *B*, **13**, 232.
[6] Graffunder and Heymann, *Z. phys. Chem.*, 1932, *B*, **15**, 377.
[7] Weiss, *Z. anorg. Chem.*, 1956, **287**, 223.
[8] O'Dwyer, *J. Mol. Spect.*, 1958, **2**, 144.
[9] Cotton, Danti, Waugh, and Fessenden, *J. Chem. Phys.*, 1958, **29**, 1427.
[10] Sheline and Pitzer, *J. Amer. Chem. Soc.*, 1950, **72**, 1107.
[11] King and Lippincott, *J. Amer. Chem. Soc.*, 1956, **78**, 4192.
[12] Stammreich, Sala, and Tavares, *J. Chem. Phys.*, 1959, **30**, 856.
[13] Edgell, personal communication.
[14] Vohler, *Chem. Ber.*, 1958, **91**, 1235.

been derived by standard group-theoretical methods. The results are presented in Tables 1 and 2. The substituent RNC has been used since it is of the type which itself has a bond lying along its molecular axis, and hence, presumably, also along the metal–ligand atom axis, which gives an easily observed and identified stretching frequency. Thus, for such ligands we require that the number of infrared active substituent stretching frequencies agree with theory in addition to having such agreement for the CO stretching frequencies. For the kind of ligand which has no characteristic group so placed that the vibrations of those in two or more co-ordinated ligands will couple, *e.g.*, R_3P, we have only the CO stretching frequencies on which to depend in drawing conclusions as to configuration.

TABLE 1. *Symmetry types and activities of certain vibrational modes in* $(R{\cdot}NC)M(CO)_4$ *species.*

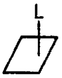
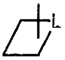
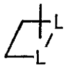
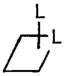
Structure	Point-group symmetry	Symmetry species and activities (R = Raman, IR = infrared)		Number of infrared-active modes	
		C≡N str.	CO str.	C≡N	CO
	C_{4v}	A_1 (IR,R)	A_1 (IR,R) B_1 (R) E (IR,R)	1	2
	C_s	A' (IR,R)	3A′ (IR,R) A'' (IR,R)	1	4
	C_{3v}	A_1 (IR,R)	$2A_1$ (IR,R) E (IR,R)	1	3
	C_{2v}	A_1 (IR,R)	$2A_1$ (IR,R) B_1 (IR,R) B_2 (IR,R)	1	4

TABLE 2. *Symmetry types and activities of certain vibrational modes in* $(R{\cdot}NC)_2M(CO)_3$ *species.*

Structure	Point-group symmetry	Symmetry species and activities (R = Raman, IR = infrared)		Number of infrared-active modes	
		C≡N str.	CO str.	C≡N	CO
	D_{3h}	A' (R) A_2'' (IR)	A_1' (R) E' (IR,R)	1	1
 	C_{2v}	A_1 (IR,R) B_2 (IR,R)	$2A_1$ (IR,R) B_1 (IR,R)	2	3
  	C_s	$2A'$ (IR,R) or A' (IR,R) A'' (IR,R)	$2A'$ (IR,R) A'' (IR,R)	2	3

An important point should be stressed about the disubstituted molecules. It will be seen in Table 2 that there are two disubstituted molecules, one derived from the TBP and the other from the RP, which have C_{2v} symmetry. Naturally they have the same selection rules and are hence completely indistinguishable by the number of bands expected in the infrared. Indeed, their indistinguishability is of a very fundamental nature. Each of them represents only one of an infinite number of structures with the same symmetry but continuously varying bond angles. Were the results to suggest such a structure, there would be no reason to expect that it should necessarily be either of these two, which happen to have angles equal to those found in the two possible unsubstituted prototypes. Indeed, it would be unlikely for this to be the case. Thus the question of whether such a C_{2v} molecule should be considered as a substituted TBP or RP has in general *no meaning.* A similar statement can be made concerning the three disubstituted models of C_s symmetry.

Results and Discussion

The experimental results obtained for the various molecules studied are presented in Table 3. Also included for convenient comparison are Vohler's data for $[(Ph_3P)_2Co(CO)_3]^{1+}$ and Seyferth and Kahlen's [15] data for $(CH_3)_3Si\cdot NCFe(CO)_4$ and $(CH_3)_3Ge\cdot NCFe(CO)_4$.

TABLE 3. *Observed spectra in the* CO *and* C≡N *stretching regions for* $LM(CO)_4$ *and* $L_2M(CO)_3$ *molecules and ions.*

		Observed bands [a] (cm.$^{-1}$)	
Compound	Medium	CN stretches	CO stretches
$(C_6H_5)_3PFe(CO)_4$	$CHCl_3$		2059(3), 1978(3), 1938(10)
	CCl_4		2059(3), 1984(3), 1946(10)
	CS_2		2063(3), 1982(3), 1943(10)
$[(C_6H_5)_3P]_2Fe(CO)_3$	$CHCl_3$		1887
	CS_2		1886
$(CH_3\cdot NC)Fe(CO)_4$	$CHCl_3$	2218(3)	2072(3), 1996(3), 1967(10)
	CCl_4	2210(3)	2072(3), 2002(4), 1969(10)
	CS_2	2208(4)	2068(3), 1997(4), 1967(10)
$(CH_3\cdot NC)_2Fe(CO)_3$	$CHCl_3$	2170(7)	*2009(0·5)*, 1925(10)
	CS_2	~2160(4)	*2009(0·5)*, 1927(10)
$[(CH_3)_3C\cdot NC]Fe(CO)_4$	$CHCl_3$	2186(2)	2066(2), 1997(2), 1966(10)
	CCl_4	2185(2)	2069(3), 2004(3), 1972(10)
	CS_2	~2160(4, vb)	2067(3), 2000(3), 1970(10)
	CCl_4(CaF_2 prism)	2211(3)	2069(3), 1998(3), 1970(10)
$[(CH_3)_3C\cdot NC]_2Fe(CO)_3$	$CHCl_3$	2139(6), 2090(vw, sh)	*2006(0·6)*, 1923(10)
	CCl_4	2134(6), 2090(vw, sh)	*2009(0·7)*, 1927(10)
	CS_2	2133(7), 2082(vw, sh)	*2005(0·6)*, 1923(10)
$(C_2H_5\cdot NC)_2Fe(CO)_3$	$CHCl_3$	2155(4)	*2004(0·5)*, 1922(10)
	CCl_4	2149(5)	*2012(0·6)*, 1932(10)
	CS_2	~2140(3, vb)	*2011(0·7)*, 1930(10)
$(C_6H_5\cdot NC)Fe(CO)_4$	$CHCl_3$	2175(1)	2067(3), 2003(4), 1973(10)
	CCl_4	2171(2)	2065(4), 2007(4), 1976(10)
	CS_2	2172(2)	2062(4), 2003(4), 1972(10)
$(C_6H_5\cdot NC)_5Co(ClO_4)$	$CHCl_3$	2157(5), 2120(10)	
$[(CH_3)_3Si\cdot NC]Fe(CO)_4$	$CHCl_3$	2132	2050, 1996, 1972
$[(CH_3)_3Ge\cdot NC]Fe(CO)_4$ [b]	$CHCl_3$	2135	2057, 1997, 1968
$(CH_3)_3Si\cdot NC$ [b]	$CHCl_3$	2198	
$(CH_3)_3Ge\cdot NC$ [b]	$CHCl_3$	2197	
$\{[C_6H_5)_3P]_2Co(CO)_3\}^{1+}$	$COMe_2$		2007
		C≡N *Frequencies in free* RN≡C	
$(CH_3)_3C\cdot NC$	CCl_4	2145(10), ~2115(vw, sh), 2079(1)	
	CS_2	2141(10), ~2112(vw, sh), 2078(1)	
$C_6H_5\cdot NC$	CCl_4	2138	
$CH_3\cdot NC$ [d]	gas	2166	
$C_2H_5\cdot NC$	$CHCl_3$	2160	

[a] Numbers in parentheses following frequencies indicate relative intensities (areas); vw = very weak; vb = very broad; sh = shoulder. [b] Seyferth and Kahlen, *J. Amer. Chem. Soc.*, in the press. [c] Vohler, *Chem. Ber.*, 1958, **91**, 1235. [d] Williams, *J. Chem. Phys.*, 1956, **25**, 656.

It will be seen that for all the monosubstituted compounds there are three CO stretching bands, and, for the isocyanide compounds, also one C≡N stretching band. Inspection of Table 1 shows that the following conclusions may be drawn.

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[15] Seyferth and Kahlen, *J. Amer. Chem. Soc.*, in the press.

(1) Since the C_{4v} structure derived from an RP should have only two CO bands, this structure is eliminated conclusively.

(2) The spectra agree with expectation for the C_{3v} model but lack a band required by both the C_s and the C_{2v} models. While the last two cannot be said to be thus conclusively eliminated, since it is always possible for a band to go undected because of poor resolution, or of accidental near-degeneracy such that no available optics could provide the necessary resolution or anomalous weakness of the band, the C_{3v} model is strongly favoured. Since the spectrum of $Bu^t \cdot NCFe(CO)_4$ appears exactly the same with calcium fluoride or sodium chloride optics, it seems unlikely that a fourth band has gone unresolved here, since calcium fluoride should, under the experimental conditions, afford resolution of 4—6 cm.$^{-1}$. It should also be noted that, while we may find it convenient to consider the C_{3v} structure to be derived from a TBP by substitution at one axial position, it is not necessary that the three remaining equatorial CO groups be coplanar with the iron atom after substitution.

For the disubstituted compounds, the results may be taken to favour the D_{3h} model, derived from a TBP by substitution at both axial positions. Our results for $(Ph_3P)_2Fe(CO)_3$ and Vohler's for $[(Ph_3P)_2Co(CO)_3]^{1+}$ agree perfectly with expectation for this structure, as Vohler has already noted concerning his own results. It appears unlikely that two of the three bands required by the C_{2v} and C_s structures would escape detection.

For the isocyanide compounds, the results also suggest the correctness of the D_{3h} model, but here there is possibly some uncertainty because of the presence in every case of an additional, weak CO band at 2005—2012 cm.$^{-1}$. This band is always more than a power of ten weaker than the strong band at 1920—1930 cm.$^{-1}$. Its presence despite a structure of D_{3h} symmetry, or nearly so, can be explained in at least two ways. First, it could be a combination or overtone band which has gained intensity by Fermi resonance with the strong fundamental. Secondly, it could be the A_1', totally symmetric CO stretching mode which gains a little intensity in the infrared because non-linearity of the C–N–R group slightly perturbs the D_{3h} symmetry of the $CN \cdot Fe(CO)_3 \cdot NC$ grouping.

We consider it likely that the presence of this weak band can be explained in one of the above ways, although we have been unable to devise any proof of either. If it is agreed that this weak band is not a fundamental, then the results for the disubstituted compounds containing isocyanides, like those containing triphenylphosphine, appear to have TBP configurations of the metal ligand bonds with substituents at the axial positions. A reasonably certain proof, or disproof, as the case may be, should be obtained by work now in hand on the dipole moments of these compounds and also from infrared study of compounds of the type $(diphosphine)Fe(CO)_3$ in which only a C_{2v} or a C_s structure is possible.

The appearance of two C≡N stretching frequencies in $[(Ph \cdot NC)_5Co]^{1+}$ supports the assumption that this ion has a TBP configuration for which two C≡N stretching modes are expected, whereas three are expected for an RP configuration. However, the resolution of a rock-salt prism at this frequency is perhaps only 10—15 cm.$^{-1}$ and the above conclusion should be accepted only with this reservation in mind. We hope to re-examine this spectrum under better resolution as soon as possible.

There is one other feature of the data in Table 3 which merits comment. It will be noted that for the compounds $(CH_3)_3M \cdot NCFe(CO)_4$, where M = C, Si, or Ge, the NC frequency when M = C is ~40 cm.$^{-1}$ *higher* than in the free ligand, whereas, for M = Si and Ge, the N≡C frequency in the complex is ~60 cm.$^{-1}$ *lower* than in the free ligand. This presumably means that, whereas complex-formation raised the NC bond order for $(CH_3)_3C \cdot NC$, it lowers it for $(CH_3)_3Si \cdot NC$ and $(CH_3)_3Ge \cdot NC$. Mechanisms by which raising and lowering of the NC bond order may occur can be easily formulated in the concepts of valence bond theory, beginning with the generally accepted view that isocyanides may be regarded as resonance hybrids of (I) and (II). Clearly, when the carbon atom is attached

$$\text{(I)}\quad R-\overset{+}{N}\equiv\overset{-}{C}: \longleftrightarrow R-\ddot{N}=C: \quad\text{(II)}$$

to a metal atom so that negative charge is drained from the carbon atom, there will be a tendency for the contribution of (I) to increase, thus increasing the NC bond order.

As with co-ordinated CO we might also expect back-donation of electrons from metal-atom $d\pi$ orbitals which would tend to lower the NC bond order, in opposition to the inductive effect just discussed. It must be concluded that for $(CH_3)_3C\cdot NC$, the inductive effect dominates, the net result being an increase in NC bond order, while for $(CH_3)_3Si\cdot NC$ and $(CH_3)_3Ge\cdot NC$ the back-donation dominates, the net result being a lowering of the NC bond order. We believe that there is a simple qualitative explanation for the greater extent of back-donation with $(CH_3)_3Si\cdot NC$ and $(CH_3)_3Ge\cdot NC$ than with $(CH_3)_3C\cdot NC$.

This explanation is best framed in molecular orbital terms. In the ≡CNC′ system there are, in a given plane, two $p\pi$ atomic orbitals, one each on C′ and N, and two electrons to be housed in them. These two orbitals combine to give a bonding MO and an antibonding MO, with the electrons occupying the former. In the ≡CNC′Fe system there are, in a given plane, now three π orbitals, N$p\pi$, C′$p\pi$, and Fe$d\pi$, and four electrons to be housed. In general the combination of three orbitals such as these leads to a bonding MO, a non-bonding MO, and an antibonding MO. The four electrons would then occupy the first two. Thus, when ≡CNC′ and $Fe(CO)_x$ are separated we have a filled bonding MO (on the isocyanide), a filled non-bonding AO (on Fe), and an empty antibonding MO (on the isocyanide). When ≡CNC′ and $Fe(CO)_x$ are combined we still have filled bonding and non-bonding orbitals and an empty antibonding orbital. So far as the total energy of the π electrons is concerned, approximately no stabilization is to be gained by interaction between the NC′ π-MO's and the metal $d\pi$ orbital.

However, for $(CH_3)_3Si\cdot NC$ and $(CH_3)_3Ge\cdot NC$, where Si and Ge have empty $d\pi$ orbitals, interaction with metal $d\pi$ orbitals can be expected to stabilize the entire group of π electrons. For the ≡MNC (M = Si, Ge) system (again considering π electrons and orbitals in only one plane) there are two electrons in a bonding orbital, an empty non-bonding orbital, and an empty antibonding orbital, and on $Fe(CO)_x$ there is a filled non-bonding $d\pi$ orbital. Now on combining four π orbitals there result, in general, two bonding orbitals and two anti-bonding orbitals, and in this case, both bonding orbitals will be occupied. Thus there is a net stabilization of the system of four π electrons by the interaction. This provides more driving force for back-donation, with consequent lowering of the NC bond order, than there is in the ≡CNC′ case.

EXPERIMENTAL

Microanalyses are by S. M. Nagy, M.I.T., and Schwartzkopf Microanalytical Laboratories, Woodside, N. Y. Spectra were obtained on a Perkin–Elmer Model 21 double-beam spectrometer; a rock salt prism was used, except in one instance where a check was made by using a Baird spectrometer equipped with a fluorite prism.

$(Ph_3P)Fe(CO)_4$ *and* $(Ph_3P)_3Fe(CO)_3$.—These compounds were mentioned by Reppe and Schwekendiek,[16] who stated that they were obtained by direct reaction of triphenylphosphine with iron pentacarbonyl, but gave no further details. Our procedure was as follows: triphenylphosphine (2·9 g.) and iron pentacarbonyl (1·6 ml.) were placed in a Carius tube which was then cooled, evacuated, and sealed. During 3 hours' heating at 110°, pressure developed and a yellow solid was produced. This was washed with ether and dissolved in benzene, and the solution was filtered. The benzene was then taken off *in vacuo*, and the residue sublimed. At ~180° a sublimate having m. p. (sealed tube) 201—202° (decomp.) was obtained [Found: C, 62·7; H, 4·6. Calc. for $(Ph_3P)Fe(CO)_4$: C, 61·4; H, 3·5%)]. Reppe [16] gives 203° as the m. p. of $(Ph_3P)Fe(CO)_4$. The residue from the sublimation, recrystallized from benzene, had m. p. 260° (decomp.) [Found: C, 70·4; H, 4·7. Calc. for $(Ph_3P)_2Fe(CO)_3$: C, 70·6; H, 4·55%] (Reppe gives 270°).

The isocyanide compounds containing $CH_3\cdot NC$, $C_2H_5\cdot NC$, and $C_6H_5\cdot NC$ were all prepared according to Hieber and von Pigenot [17] and had the properties described by them (analyses for C and H were very satisfactory).

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[16] Reppe and Schwekendiek, *Annalen*, 1948, **560**, 104.

[17] Hieber and von Pigenot, *Chem. Ber.*, 1956, **89**, 193.

The t-butyl isocyanide derivatives are new. t-Butyl isocyanide was prepared in a manner similar to that described by Nef.[18] The yield was ~18%.

Butylisocyanideiron tetracarbonyl. Iron pentacarbonyl (0·42 ml., 3·13 mmoles) and t-butyl isocyanide (0·34 ml., ~3·2 mmoles) were heated in vacuum on a steam-bath for 3 hr., the tube being cooled to −78° every hour, and the carbon monoxide pumped out. Reaction was then complete (no further carbon monoxide evolution), and volatile contaminants were removed by evacuation at −78°, and the product sublimed *in vacuo* on to a cold finger held at −70° as pale yellow crystals, m. p. 53·5—54·5° (0·630 g.). The *compound* is sensitive to air and light, although considerably more stable than the corresponding methyl isocyanide compound. It is very soluble in common organic solvents (Found: C, 42·6; H, 3·9; N, 5·9. $C_9H_9NO_4Fe$ requires C, 43·1; H, 3·6; N, 5·6%).

Di-(t-butylisocyanide)iron tricarbonyl. Iron pentacarbonyl (1·9 ml., 14 mmoles) and t-butyl isocyanide (3·8 ml., ~38 mmoles) were heated in an evacuated tube on the steam-bath, carbon monoxide being pumped off hourly as before. Reaction was complete in 7 hr. Volatile products were removed *in vacuo* at 50°, and the residue was extracted with boiling light petroleum (b. p. 60—80°) from which the *product* crystallized as yellow needles, m. p. 98—98·5° (3·5 g.) (Found: C, 50·8; H, 6·0; N, 9·4. $C_{13}H_{18}N_2O_3Fe$ requires C, 51·1; H, 5·9; N, 9·2%). The compound is fairly unstable toward air and light and thermally. It dissolves readily in common organic solvents and the solutions decompose fairly rapidly in presence of air.

$(C_6H_5{\cdot}NC)_5Co(ClO_4)$ was prepared according to Malatesta and Sacco.[19]

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[18] Nef, *Annalen*, 1899, **309**, 154.

[19] Malatesta and Sacco, *Z. anorg. Chem.*, 1953, **273**, 247.