certain than the others because the absorbance values in these two instances were very low (~0.09). Thus the values for K calculated from these data are much more affected by the small uncertainty in the blank correction than are the others. On the basis of this consideration it appears proper to conclude that within the limits of accuracy of the measurement K is independent of $I(SCN)_2^-$ concentration.

The variation of K with temperature is shown in Table III. A least-squares analysis of the linear plot of log K *vs.* the reciprocal of temperature yielded a value for ΔH^* of 23.3 kcal./mole; the standard deviation of the datum was 2.3 kcal./mole. Extrapolation of the line to 25° gave a value for K of 8×10^{-5} with a 95% confidence interval of 5×10^{-5}. Attempts to measure K at room temperature were unsuccessful because of the rapid oxidative decomposition occurring under these conditions.

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Infrared Studies of Planar and Tetrahedral Inorganic Thiocyanates[1]

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Received August 16, 1965

The absorption frequencies, half-band widths, and integrated intensities in the 2100 cm.$^{-1}$ spectral region have been examined for a number of thiocyanato and selenocyanato complexes in inert solvents. A useful correlation between absorption intensity and type of coordination of the triatomic group to the metal has been ascertained. The integrated intensity of the CN stretching absorption band is in the range $0.8–2.3 \times 10^4$ M^{-1} cm.$^{-2}$ for the thiocyanates and that of the isothiocyanates is in the range $9–12 \times 10^4$ M^{-1} cm.$^{-2}$. Similar values are found for the selenocyanates. These correlations have been applied to planar and tetrahedral thiocyanates of the type $ML_2(CNS)_2$, M = Ni(II), Pd(II), Pt(II), Zn(II), and Co(II), in order to ascertain the nature of the metal–thiocyanate coordination.

Introduction

The infrared spectral behavior of the triatomic cyanate,[3] thiocyanate,[4–9] and selenocyanate[10–12] groups in their inorganic compounds has been investigated by several authors. The best known case is that of the SCN group, for which a series of useful correlations between type of coordination and infrared spectral parameters has been established.

The low-frequency skeletal stretching mode (approximating a CS stretching mode) is characteristic of the type of coordination in the absence of bidentate bridging groups: this frequency ranges from 690 to 720 cm.$^{-1}$ in the M–SCN compounds and from 780 to 860 cm.$^{-1}$ in the M–NCS compounds.[7]

The high-frequency stretching mode (approximating a CN stretching mode) at 2050–2130 cm.$^{-1}$ lies generally higher for the M–SCN compounds than for the M–NCS compounds; however, except for the case of linkage isomers, it may not be characteristic because overlap can often occur.[8–9] The value of the CN stretching frequency has been widely used as a diagnostic criterion for the existence of M–SCN–M bridges. In compounds where SCN functions as a bridge, this frequency lies some 30–60 cm.$^{-1}$ higher than in the case of terminal SCN groups.[13]

These correlations have often been used to establish the type of coordination of the SCN group, and their correctness has received further support recently by direct X-ray structural evidence.[14–15]

Similar correlations appear to be valid also for the selenocyanato complexes, although the existing information is much less extensive for this class of compounds.[11–12]

Using these infrared diagnostic criteria, it was possible to show[7] that in complexes of the type $L_2Pt(CNS)_2$[16] and $L_2Pd(CNS)_2$ the type of bonding (M–SCN or M–NCS) can change depending on the nature of the other ligands in the complex. As a consequence of this observation, Turco and Pecile suggested that it should be possible to obtain linkage isomers, by a proper choice of ligands.[7] The first case of such linkage iso-

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(1) This investigation was supported by the Italian "Consiglio Nazionale delle Ricerche" (C.N.R., Rome).

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(16) The (CNS) symbol is used to indicate that the type of metal–ligand bonding is not specified or identified.

mers has been reported by Basolo, *et al.*,[17] who succeeded in preparing the M–NCS and M–SCN isomers of the compound $Pd[As(C_6H_5)_3]_2(CNS)_2$. Another case of linkage isomerism has been further reported for the compound $Mn(CO)_5(CNS)$.[18]

Several factors have been considered in order to explain the way NCS^- binds to a given metal and the reasons for the change from M–SCN to M–NCS bonds. In the case of the platinum(II) complexes of the type $PtL_2(CNS)_2$, it has been suggested that good π-bonding ligands should favor M–NCS bonding.[7] Wojcicki and Farona[18] have stressed the importance of the effective charge on the metal in discussing the manganese(I) compound $Mn(CO)_5(CNS)$. Finally, the importance of steric factors has been duly considered by Basolo.[19,20]

In order to rationalize the correlations existing between spectral parameters and type of coordination, the infrared spectra in solution of thiocyanato and selenocyanato complexes representative of the basic types known have been carefully measured in the CN stretching region. The results of this investigation have been applied to a number of planar and tetrahedral thiocyanates of uncertain coordination, with the aim to establish the type of metal–thiocyanate bonding and to elucidate the geometrical configuration of some isomeric forms.

Experimental Section

Preparation of Complexes.—The complexes used in this investigation were all known compounds and were prepared by the methods reported in the literature. Carbon, hydrogen, nitrogen, and metal analyses were performed on all samples to be certain of identity and purity. The compounds listed in Table IV were also characterized by means of molecular weight and conductance measurements to make sure that they are present as nonionic monomeric species in the solvents used.

Conductance measurements showed that the complexes $Pd(CNCH_3)_2(SCN)_2$ and $Pd[CN(i\text{-}C_3H_7)]_2(SCN)_2$ are non electrolytes ($\Lambda_M < 3$ mhos) in 10^{-3} M nitromethane solution.

References to the methods of preparation are as follows: $[N(C_2H_5)_4]_2[Co(NCSe)_4]$,[11] $Co[P(C_6H_{11})_3]_2X_2$,[21] $Co[OP(C_6H_{11})_3]_2X_2$,[21] $Co[P(C_6H_5)_3]_2X_2$,[22] $Ni[P(C_6H_5)_3]_2X_2$,[23] $Ni[P(i\text{-}C_3H_7)_3]_2X_2$,[24] $Zn[P(C_2H_5)_3]_2X_2$,[25] $Pd(CNR)_2X_2$,[25] $R = CH_3$, $i\text{-}C_3H_7$ ($X = Cl$, Br, CNS). *trans*- and *cis*-$Pt[P(C_2H_5)_3]_2(NCS)_2$ and *trans*-$Pt[As(C_2H_5)_3]_2(NCS)_2$ were prepared by metathetical reaction from the corresponding chloro derivatives; $Pd(PR_3)_2X_2$ ($R = i\text{-}C_3H_7$, C_6H_{11}, C_6H_5) were prepared by essentially the same method. A solution of K_2PdX_4 in water ($X = Cl$) or acetone ($X = NCS$) was mixed with an acetone solution of a stoichiometric amount of the phosphine ligand.

Infrared Spectra.—All spectra were run on a Perkin-Elmer Model 21 double-beam spectrometer equipped with a rock salt prism. Frequencies are believed to be accurate to ±5 cm.$^{-1}$. The samples were examined either as solid Nujol mulls or as freshly prepared solutions in fixed thickness cells with calcium fluoride windows and Teflon spacers.

The integrated intensity A, in units of M^{-1} cm.$^{-2}$, was obtained by Ramsay's method of direct integration.[26] The Beer's law plot was checked to be straight and go through the origin.

Results and Discussion

Free NCX^- Ions and $M_m(CNX)_n^{(n-m)-}$ Complexes.—In Table I are listed the parameters of the absorption band of the SCN^- and $SeCN^-$ ions in the 2060–2080 cm.$^{-1}$ region. The fundamental vibrational mode corresponding to the absorption in this frequency region is the asymmetric stretching vibration (approximately a CN stretch) and is indicated as $\nu_{as}(NCX)$.[4,10] These data are presented primarily to provide a point of reference in interpreting the absorption patterns of the coordinated ions. Measurements were made using several solvents in order to assure that no anomalously solvent-dependent values were used. It may be seen that there is an important change of the absorption parameters in going from nonhydroxylic to hydroxylic solvents. This is clearly shown by the increase of the value of the integrated intensity A in water and ethanol.

This strong effect can be attributed to hydrogen-bonding interaction of the type XCN···H—O.[8]

Similar conclusions can be derived from the data of Table I with regard to the $SeCN^-$ ion.

TABLE I

FREQUENCY, APPARENT HALF-BAND WIDTH ($\Delta\nu_{1/2}$), AND INTEGRATED INTENSITY (A) OF THE INFRARED ABSORPTION AT 2060–2080 CM.$^{-1}$ FOR THE SCN^- AND $SeCN^-$ IONS[a]

Compound	Solvent	ν_{as} (NCX),[b] cm.$^{-1}$	$\Delta\nu_{1/2}$, cm.$^{-1}$	ϵ_{max}, M^{-1} cm.$^{-1}$	$A \times 10^{-4}$, M^{-1} cm.$^{-2}$
KSCN	$CH_3COC_2H_5$	2060	16	760	4.4
	$HCON(CH_3)_2$	2061	16	745	4.4
	H_2O	2068	32	465	5.7
	C_2H_5OH	2068	46	425	7.2
KSeCN	$CH_3COC_2H_5$	2069	18	470	3.1
	H_2O	2078	34	342	4.3
	C_2H_5OH	2078	47	285	4.9

[a] Range of concentrations $2\text{–}5 \times 10^{-2}$ M; cell thickness 0.11 mm. (for aqueous solution 0.018 mm.). [b] NCX, X = S or Se.

In Table II the absorption parameters in the 2080–2120 cm.$^{-1}$ region of some thiocyanato and selenocyanato complexes in solution are listed. The single and symmetric absorption band is assigned to the asymmetric stretching mode $\nu_{as}(NCX)$ of the NCX coordinated group (CN stretch).[27] Chemical evidence and X-ray structural data allow one to assume with a fair degree of certainty that the type of coordination is M–NCX for compounds V–VIII[7–9] and XI,[11,12] and M–XCN for compounds I–IV[7–9] and IX and X.[11]

The observation that nitrogen-bonded complexes can be distinguished from sulfur-bonded complexes in solution by the intensity value of the CN stretching absorption was recently reported for a few cases of thiocyanate complex ions in aqueous[28] and in acetone[8]

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Table II

Frequency, Apparent Half-Band Width ($\Delta\nu_{1/2}$), and Integrated Intensity (A) of the Infrared Absorption at 2100 Cm.$^{-1}$ for Some Thiocyanato and Selenocyanato Complexes

Compound	Solvent	ν_{as} (NCS) cm.$^{-1}$	$\Delta\nu_{1/2}$, cm.$^{-1}$	ϵ_{max},^{a} M^{-1} cm.$^{-1}$	$A \times 10^{-4}$,^{a} M^{-1} cm.$^{-2}$
I $K_2Pd(SCN)_4$	$CH_3COC_2H_5$	2110	16	325	1.9
	CH_3CN	2110	15	375	2.27
II $K_2Pt(SCN)_4$	CH_3COCH_3	2112	12	477	1.8
III $K_2Hg(SCN)_4$	CH_3COCH_3	2113	17	350	2.12
	CH_3CN^d	2112	16	320	1.82
	Water^b	2112	27	420	...
IV $K_2Pt(SCN)_6$	CH_3COCH_3	2120	14	207	1.03
	CH_3CN	2125	12	202	0.85
	Water^b	2126	15	246	...
V $K_2Zn(NCS)_4$	$CH_3COCH_3^c$	2084	19	...	(8.8)
VI $[N(C_2H_5)_4]_2[Co(NCS)_4]$	$ClCH_2CH_2Cl$	2074	22	1350	10.7
	$CH_3COC_2H_5$	2077	18	1320	11.7
VII $K_3Cr(NCS)_6$	$CH_3COCH_3^c$	2094	19	...	(8.6)
	Water^b	2088	39	937	...
VIII $[NH_4][Cr(NH_3)_2(NCS)_4]\cdot H_2O$	$CH_3COC_2H_5$	2083	18	1590	...
	$HCON(CH_3)_2$	2083	18	1640	...
	CH_3CN	2083	18	1590	...
IX $K_2Hg(SeCN)_4$	CH_3COCH_3	2116	16	245	1.45
	CH_3CN	2115	15	267	1.30
X $K_2Pt(SeCN)_6$	CH_3COCH_3	2122	14	127	0.55
	CH_3CN	2123	14	166	0.62
XI $[N(C_2H_5)_4]_2[Co(NCSe)_4]$	CH_3COCH_3	2070	20	1400	9.5

[a] Calculated per mole of coordinated XCN group. [b] Values reported by Fronaeus and Larsson.[28] [c] ν and $\Delta\nu_{1/2}$ values reported by Tramer.[8] The integrated intensity is roughly evaluated from Tramer's data using the integrated intensity in $CH_3COC_2H_5$ of the free SCN ion from Table I. [d] Absorption at 2112 cm.$^{-1}$ is accompanied by a weak absorption at 2055 cm.$^{-1}$ due to a small degree of decomposition. No correction was introduced in calculating ϵ and A values.

solutions. On the other hand, the strong intensity rise of the CN stretching absorption following the isomerization R–XCN → R–NCX is well known for organic derivatives of the SCN and SeCN groups.[29,30]

The comparison of the spectral parameters of the M–SCN complexes (I–IV) with those of the M–NCS complexes (V–VIII) shows that the two types of coordination can easily be differentiated by the value of the integrated intensity A (M^{-1} cm.$^{-2}$) of the absorption per single SCN coordinated group: M–SCN, $A = 0.8\text{–}2.3 \times 10^4$; M–NCS, $A = 9\text{–}12 \times 10^4$.

The data in Table II also show that the product $\epsilon_{max} \times \Delta\nu_{1/2}$ can be used in place of the integrated intensity A, as a rough but nonequivocal indication of the type of coordination. In fact, this product is about one order of magnitude greater for the isothiocyanates than for the thiocyanates.

The same conclusions seem to be valid for the selenocyanato compounds, although the examples listed in Table II are much less numerous.

The intensity data of the CN stretching absorption provide the most valuable means of studying the type of coordination in solution. On the other hand, it has already been shown[7] that the CS stretching frequency is better for the same purpose in studies of solid compounds.

Planar Complexes of the Type $ML_2(CNS)_2$.—In Table III are listed the spectral parameters of planar complexes of nickel(II), palladium(II), and platinum(II). Inspection of the data reveals that the ν_S(NCS) frequency (approximately a CS stretch) of the mull spectra of compounds I–VIII is well within the range (780–860 cm.$^{-1}$) assigned to the isothiocyanato ligands.[7] The isothio structure is confirmed for compounds I, III, VI, and VIII in solution by the high value of the intensity parameters. Thus all of these compounds are to be considered isothiocyanato complexes in the solid state for the value of the CS stretching frequency and in solution for the observed intensity of the CN stretching absorption. Compounds IX and X appear to be of the type M–SCN.

Differentiation of M–NCS from M–SCN complexes can be complicated in the presence of *cis–trans* isomerism. In the isothiocyanates *cis-* and *trans*-$Pt[P(C_2H_5)_3]_2(NCS)_2$ (compounds VI and VII, Table III), a different set of vibrations must be considered. In the *trans* planar isomer only one vibrational mode associated with the asymmetric stretching of the two NCS groups coordinated to the metal is infrared active, namely, the out-of-phase mode. In the *cis* isomer both the in-phase and the out-of-phase vibrational modes are infrared active. The same considerations are valid for the symmetric stretching vibrational modes. Thus in the spectrum of a *cis* square-planar isothiocyanate one expects to observe two bands in both the 2100 and 800 cm.$^{-1}$ regions. In fact the spectrum of solid *trans*-$Pt[P(C_2H_5)_3]_2(NCS)_2$ exhibits one single band at 2113 cm.$^{-1}$, whereas a clear doublet (which is also present in solution) at 2116, 2107 cm.$^{-1}$ is observed in the spectrum of the *cis* compound. Similarly, one observes a single band at 855 cm.$^{-1}$ in the spectrum of the *trans* compound and a doublet at 848, 830 cm.$^{-1}$ in the *cis* compound. Furthermore, the CS stretching absorption of the *cis* compound is very weak as compared to that of the *trans* compound. This observation suggests that one must be very careful in using the CS stretching frequency as a means for differentiating isothiocyanates and thiocyanates. In fact, the intensity of this band in some cases can be very low, and therefore its assignment can occasionally be very difficult.

The differentiation between *trans* and *cis* isomers seems to be possible in solution. The *trans* isomer exhibits one band with a value of the product $\epsilon_{max} \times \Delta\nu_{1/2}$ typical of M–NCS coordination. The *cis* isomer presents a broader absorption clearly due to two bands. The product $\epsilon_{max} \times \Delta\nu_{1/2}$ (Table III) still indicates M–NCS coordination. The occurrence of two bands with a small frequency separation (~10 cm.$^{-1}$) and a relatively high $\Delta\nu_{1/2}$ value (~20 cm.$^{-1}$) might give rise, in different *cis* complexes, to a broad band instead of a clearly splitted absorption. Thus in some cases it can happen that this splitting is not clearly exhibited by *cis*-isothiocyanato complexes. However, this seems not to constitute a serious limitation for the study of the

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[29] (a) N. S. Ham and J. B. Willis, *Spectrochim. Acta*, **16**, 279 (1960); F. A. Miller and W. B. White, *Z. Elektrochem.*, **64**, 705 (1960); (b) C. Pecile and T. Tarantelli, *Ann. Chim.* (Rome), **52**, 75 (1962); C. Pecile, to be published.

[30] The following ranges of values of integrated intensity A (M^{-1} cm.$^{-2}$) can be taken as characteristic of organic compounds[29]: R–SCN, $A = 0.8 \times 10^4$; R–NCS, $A \approx 4\text{–}16 \times 10^4$; R–SeCN, $A = 0.1\text{–}0.2 \times 10^4$; R–NCSe, $A \approx 5\text{–}10 \times 10^4$.

TABLE III

INFRARED DATA FOR PLANAR $ML_2(CNS)_2$ COMPLEXES, M = Ni(II), Pd(II), AND Pt(II)

	Compound	Nujol mull or soln. in	ν_{as}(NCS), cm.$^{-1}$	$\Delta\nu_{1/2}$, cm.$^{-1}$	ϵ_{max},[a] M^{-1} cm.$^{-1}$	ν_s(NCS), cm.$^{-1}$	$A \times 10^{-4}$,[a] M^{-1} cm.$^{-2}$
I	$Ni[P(i\text{-}C_3H_7)_3]_2(NCS)_2$	Nujol	2095	...	...	860	...
		CCl_4	2094	17	1900	...	11.7
II	$Ni[P(C_6H_5)_3]_2(NCS)_2$	Nujol	2088	...	...	868	...
III	$Pd[P(i\text{-}C_3H_7)_3]_2(NCS)_2$	Nujol	2094	...	...	852 sh	...
						844	...
		CCl_4	2115	24	1560	...	14.0
IV	$Pd[P(C_6H_{11})_3]_2(NCS)_2$	Nujol	2102	...	...	845	...
V	$Pd[P(C_6H_5)_3]_2(NCS)_2$	Nujol	2092	...	...	852	...
VI	*trans*-$Pt[P(C_2H_5)_3]_2(NCS)_2$	Nujol	2113	...	...	855	...
		$CH_3COC_2H_5$	2112	26	705	...	6.7
VII	*cis*-$Pt[P(C_2H_5)_3]_2(NCS)_2$	Nujol	2116	...	...	848	...
			2107	...	...	830	...
		$CH_3COC_2H_5$	2118[b]	20[b]	1270[b]	...	4.65[b]
			2102[b]	28[b]	1500[b]	...	9.55[b]
VIII	*trans*-$Pt[As(C_2H_5)_3]_2(NCS)_2$	Nujol	2114	...	...	855	...
		$CH_3COC_2H_5$	2116	24	1340	...	11.8
IX	$Pd(CNCH_3)_2(SCN)_2$[c]	Nujol	2111	...	...	700	...
		$CHCl_3$	2124	16	255	...	1.34
X	$Pd[CN(i\text{-}C_3H_7)]_2(SCN)_2$[d]	Nujol	2113	...	...	700	...
		$CHCl_3$	2122	16	322	...	1.61
		C_6H_6	2125	12	305	...	...

[a] Calculated per mole of coordinated SCN group. [b] Values obtained from graphic resolution. The observed values are 2106, 2113 cm.$^{-1}$; ϵ_{max} 2057, 1980 M^{-1} cm.$^{-1}$; $\Delta\nu_{1/2}$ total 38 cm.$^{-1}$. [c] The ν(NC) of the isonitrile ligand are observed at 2265 cm.$^{-1}$ (Nujol) and 2267 cm.$^{-1}$ ($CHCl_3$). ν(NC) for CH_3NC in n-C_7H_{16} was observed at 2168 cm.$^{-1}$. [d] The ν(NC) of the isonitrile ligand are observed at 2245 cm.$^{-1}$ (Nujol) and 2240 cm.$^{-1}$ ($CHCl_3$ and C_6H_6). ν(NC) for i-C_3H_7NC in C_6H_6 was observed at 2140 cm.$^{-1}$.

type of coordination of the NCS group. A similar situation exists in the case of tetrahedrally coordinated $ML_2(NCS)_2$ complexes (*vide infra*).

The spectra in the solid state of the isocyanide complexes IX and X in the range 2265–2244 cm.$^{-1}$ exhibit one band corresponding to the NC vibrational stretching mode of the isocyanide ligand R–NC. The frequency of this band in the complexes listed in Table III is about 100 cm.$^{-1}$ higher than that of the free ligands. It has already been noted[31] that coordination of the isocyanide carbon to a metal ion must lead to a rise in frequency, because the effect of the positive charge of the metal will be to increase the NC bond order. Provided other opposing actions, such as back donation, are small, this electrostatic effect predominates and a net rise in the NC stretching frequency will be observed.[31] Thus, the substantial rise (100 cm.$^{-1}$) of this frequency can be taken as an indication that aliphatic isocyanides are poor π ligands for palladium(II) thiocyanates. Unfortunately this conclusion is of little help in discussing the importance of electronic and/or steric factors in determining the choice of a metal–sulfur coordination in these complexes.[20] In fact in the present case Pd–SCN bonding is in accordance with the point of view which assesses the importance of π bonding in M–NCS coordination,[7] but it also agrees with the assumption that in the absence of steric hindrance the more hindered M–SCN bonding may be favored.[19,20] In fact the small size of the CN–R group operates in the same direction as does its poor π-bond character.

Tetrahedral Complexes of the Type $ML_2(CNS)_2$.—The infrared behavior of these complexes is well exemplified by the spectra of the compounds $Zn[P(C_2H_5)_3]_2(CNS)_2$, $Co[OP(C_6H_{11})_3]_2(CNS)_2$, and $Co[P(C_6H_{11})_3]_2(CNS)_2$, Table IV.

TABLE IV

INFRARED DATA FOR TETRAHEDRAL $L_2M(CNS)_2$ COMPLEXES; M = Zn(II) AND Co(II)[a]

Compound	Nujol mull or soln. in	ν_{as} (NCS), cm.$^{-1}$	$\Delta\nu_{1/2}$, cm.$^{-1}$	ϵ_{max},[b] M^{-1} cm.$^{-1}$	ν_s (NCS), cm.$^{-1}$
$Zn[P(C_2H_5)_3]_2(NCS)_2$	Nujol	2085 sh	...	...	836
		2064			
	$ClCH_2CH_2Cl$	2075 sh	...		...
		2062	32[c]	1130	
$Co[OP(C_6H_{11})_3]_2(NCS)_2$	Nujol	2068 v bd	...	...	n.a.
	$ClCH_2CH_2Cl$	2080 sh	...		
		2066	27[c]	1110	
$Co[P(C_6H_{11})_3]_2(NCS)_2$	Nujol	2065	...	...	n.a.
		2042			
	$ClCH_2CH_2Cl$	2060 sh	...		...
		2052	30[c]	1150	

[a] sh, shoulder; v bd, very broad; n.a., not assigned. [b] Calculated per mole of coordinated SCN group. [c] $\Delta\nu_{1/2}$ values of the absorption peak obtained from graphic resolution; the integrated intensity values were not calculated.

The zinc compound $Zn[P(C_2H_5)_3]_2(CNS)_2$ is monomeric in dichloroethane. This shows that the compound is tetrahedral in solution since the two possible configurations of a zinc complex with monodentate ligands are tetrahedral or octahedral.

In the case of the complexes $Co[P(C_6H_{11})_3]_2(CNS)_2$ and $Co[OP(C_6H_{11})_3]_2(CNS)_2$ electronic spectra and magnetic susceptibility data clearly indicate that these compounds are tetrahedral both in the solid state and in solution. Also, the compounds were found to be monomeric in solution.[21]

Comparison of the spectra of $Zn[P(C_2H_5)_3]_2X_2$ (X = CNS, Cl, Br) in Nujol mulls shows that a band at 836 cm.$^{-1}$ is characteristic of the compound $Zn[P(C_2H_5)_3]_2$-

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(31) F. A. Cotton and F. Zingales, *J. Am. Chem. Soc.*, **83**, 351 (1961).

$(NCS)_2$. The value of this frequency, assigned to ν_s (NCS), clearly indicates a Zn–NCS structure. The same spectral inspection for the cobalt(II) complexes $Co[P(C_6H_{11})_3]_2X_2$ and $Co[OP(C_6H_{11})_3]_2X_2$ does not permit one to locate absorption bands characteristic of coordinated NCS groups in the 690–900 cm.$^{-1}$ region. This can be easily understood since the spectrum of $Zn[P(C_2H_5)_3]_2(NCS)_2$ shows that the intensity of the CS band is very low.

Thus the low intensity of the CS stretching absorption and the probable overlap with the absorption bands of the partner ligands $[P(C_6H_{11})_3$ and $OP(C_6H_{11})_3]$ does not permit the localization of the CS band in the cobalt complexes under discussion. With the tetrahedral complexes $ML_2(NCS)_2$[32] one is faced with the same difficulty already encountered with the *cis* square-planar complexes of the same symmetry.

The low intensity of the CS band may have been the origin of a wrong interpretation of the spectrum of $Co[P(C_6H_5)_3]_2(CNS)_2$. Assignment of a band at 760 cm.$^{-1}$ to the CS stretching has led to the attribution of a thiocyanate structure to this compound.[22] However, comparison of the spectra of $Co[P(C_6H_5)_3]_2Cl_2$ and $Co[P(C_6H_5)_3]_2Br_2$ with the spectrum of $Co[P(C_6H_5)_3]_2(NCS)_2$ shows that the presence of a low-intensity CS stretching band cannot be ruled out in the 830 cm.$^{-1}$ region. Both in the 760 and 830 cm.$^{-1}$ regions absorption bands typical of the $P(C_6H_5)_3$ ligand are present, and therefore the assignment of a low-intensity band in these regions is very difficult.

Again, intensity measurements in solution in the CN stretching region can offer the basis for a better diagnostic criterion on the type of coordination. In this region one observes a doublet at 2085, 2064 cm.$^{-1}$ for the solid $Zn[P(C_2H_5)_3]_2(NCS)_2$. This splitting is presumably due to the in-phase and out-of-phase asymmetric stretching vibration of the two NCS groups tetrahedrally coordinated to zinc. A similar doublet is observed for the cobalt(II) complexes discussed here. The absorption bands in the 2100 cm.$^{-1}$ region of the zinc and cobalt complexes in $ClCH_2$–CH_2Cl solution are strongly asymmetric on the side of the high frequencies. This can be explained as due to a doublet structure as found for the solid samples. The value of $\epsilon_{max} \times \Delta\nu_{1/2}$ for all of these complexes (Table IV) is in the range found for M–NCS coordination (Table II).

The results presented here are believed to be a useful basis for a further wide application to studies in solution on the coordination of triatomic groups to metal ions.

Acknowledgments.—The author wishes to express his appreciation to Professor A. Turco for the revision of the manuscript and for helpful discussions. The technical assistance of Miss Franca Marzola is gratefully acknowledged.

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[32] Detailed structural discussion is not the aim of the present work. To suggest an explanation of the CN stretch splitting a C_{2v} symmetry is assumed for these tetrahedral complexes.

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A Study of the Thermal Decomposition of Some Complex Oxalates of Iron(III) Using the Mössbauer Effect[1]

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Received September 30, 1965

Mössbauer spectra were measured at room temperature for the compounds $Fe_2(C_2O_4)_3 \cdot 6H_2O$, $Ba_3[Fe(C_2O_4)_3]_2 \cdot 8H_2O$, and $Sr_3[Fe(C_2O_4)_3]_2 \cdot 2H_2O$. Values of the isomer shift relative to $Cu(Co^{57})$ are +0.15, +0.03, and +0.16 mm./sec. and the quadrupole splittings are 0.57, 0.32, and 0.44 mm./sec., respectively. The alkaline earth compounds were heated to 1000°, and the iron(III) oxalate was heated to 600° in air at an approximate rate of 200°/hr. Samples were extracted at various temperatures and quenched, and their Mössbauer spectra were measured. The changing oxidation state of iron is clearly followed through the course of the decompositions. For example, the oxidation state of iron in the strontium compound is converted completely to +2 at 300° and reverts to +3 by 400°. At 700° a significant percentage is present as +4 which is gradually reduced to +3 with increasing temperature. The nature of these decompositions is discussed, and the results of the Mössbauer measurements are correlated with previous work on the thermal analysis of these materials. The iron(III) oxide formed in the early stages of the decomposition exhibits superparamagnetism.

Introduction

Recent investigation of the thermal decomposition of barium and strontium trisoxalatoferrates(III) and iron(III) oxalate suggests that frequent changes in the oxidation state of the iron atom occur during the decomposition.[2] Thermal analysis techniques yield only indirect evidence of such changes. The Mössbauer effect, however, can be used to obtain a more direct indication of the valence state of the iron atom. Mössbauer parameters have been well established for the

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[1] Presented in part at the Symposium on Mössbauer Effect, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 5, 1965.

[2] P. K. Gallagher, *Inorg. Chem.*, **4**, 965 (1965).