is clearly observed in the oxochloro complexes. Secondly, one M–Cl stretching band was found in the oxochloro compounds and, analogously, one M–Br stretching is expected in the oxobromo complexes. Doubtless, these two modes, occurring so nearly at the same frequencies, will be strongly mixed.

Br–M–Br deformation frequencies are found at 110–140 cm.$^{-1}$ and are considerably higher than those observed in the few hexabromo complexes investigated.[3,4]

Of the three infrared-active M–Cl stretching modes expected, only a single broad band is observed, generally with one shoulder. It is likely that the three bands are contained within this envelope. The three M–Cl stretching frequencies of $[PtCl_6]^{2-}$ may be quoted for the sake of comparison: 320 cm.$^{-1}$ (E_g), 344 cm.$^{-1}$ (A_{1g}), and 340 cm.$^{-1}$ (F_{1u}).[10] The situation in the oxobromo complexes is not so clear. If the bands at *ca.* 200 cm.$^{-1}$ are assigned to the M–O rocking mode, a single M–Br stretching band without shoulders is found in all complexes except $Rb_2[MoOBr_5]$.

All three expected Cl–M–Cl bending bands were found (except in $Cs_2[MoOCl_5]$). As one of these is at 85 cm.$^{-1}$, it is expected that one of the Br–M–Br deformation bands will be outside the range investigated. Indeed two bands were found for the niobium and tungsten bromo complexes, but with molybdenum three bands were observed.

It appears, therefore, that the observed spectra of the oxohalo complexes are never in complete agreement with what is expected for an ion of C_{4v} symmetry, even though this symmetry is beyond reasonable doubt. Site symmetry splitting, accidental degeneracy, or exceptionally weak band intensities may all operate to cause this discrepancy.

It is interesting to compare the frequencies of the oxohalo complexes with the analogous ones reported for other complexes. The M–Cl stretching frequencies in the oxochloro complexes are lower than those of the corresponding hexachloro complexes with the central metal ion in the same oxidation state. In fact M–Cl stretching bands are found at 309 and 320 cm.$^{-1}$ in $Cs_2[WOCl_5]$ and $Cs_2[NbOCl_5]$, respectively, while the same bands are at 329 and 333 cm.$^{-1}$ in $[(C_2H_5)_4N][WCl_6]$ and $[(C_2H_5)_4N][NbCl_6]$. On the other hand, these frequencies are close to the M–Cl stretching frequencies in the hexachloro complexes with the central metal ion in the oxidation state +4. The values are: 308 and 325 cm.$^{-1}$ for $Cs_2[WCl_6]$ and $Cs_2[MoCl_6]$, 309 and 329 cm.$^{-1}$ for $Cs_2[WOCl_5]$ and $Cs_2[MoOCl_5]$.

The Cl–M–Cl bending frequencies of the oxochloro complexes correspond to those found for the hexachloro complexes. The Br–M–Br bending frequencies are found between 110 and 140 cm.$^{-1}$, compared with the reported Br–M–Br bending frequencies of 60 cm.$^{-1}$ in $Cs_2[WBr_6]$ and 78 cm.$^{-1}$ in $K_2[PtBr_6]$. One might think that the bands found at about 130 cm.$^{-1}$ could correspond to the first overtones of the fundamentals located at 60–70 cm.$^{-1}$. We have then measured the spectra of $Rb_2[MoOBr_5]$ and $Cs_2[MoOBr_5]$ down to 70 cm.$^{-1}$. A rather broad band is observed at 72 cm.$^{-1}$ in $Rb_2[MoOBr_5]$. Since this band is less intense than those observed at 132 and 119 cm.$^{-1}$, these two bands cannot be overtones of the former one. Moreover, no absorption is observed in the range 100–70 cm.$^{-1}$ in the analogous cesium salt, while the absorption bands assigned as Br–M–Br bendings have the same frequencies in the two compounds. Probably the band at 72 cm.$^{-1}$ in $Rb_2[MoOBr_5]$ corresponds to a lattice vibration.

Acknowledgment.—Thanks are expressed to Professor L. Sacconi for having suggested this problem and for his interest. Acknowledgment is made to the Italian "Consiglio Nazionale delle Ricerche" for financial support.

[10] L. A. Woodward and J. A. Creighton, *Spectrochim. Acta*, **19**, 775 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA

A Thiocyanate Complex of Iodine(I)[1,2]

BY CALVIN LONG AND D. A. SKOOG

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It has been shown that a complex having the probable formula $I(SCN)_2^-$ is formed by oxidation of iodide ion or elemental iodine in solutions containing potassium thiocyanate. Hydrogen peroxide or potassium iodate effect nearly quantitative conversion of the iodine to the complex form. The properties of solutions of $I(SCN)_2^-$ are described and values for the equilibrium quotient for the reaction $I(SCN)_2^- \rightleftharpoons I^- + (SCN)_2$ are reported at various temperatures.

In an earlier paper,[3] it was postulated that a rather stable complex, I_2SCN^-, is formed when iodine is dissolved in solutions of thiocyanate ion. This complex absorbs strongly in the ultraviolet region, having a typical charge-transfer band with a maximum at 303 mμ (ϵ_{max} 42,900). It was noted that exposure of solutions of this complex to bright sunlight resulted in a marked increase in the absorbance in the ultraviolet region,

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[1] Support for this work by the National Science Foundation (Research Grant NSF G-22583) is gratefully acknowledged.

[2] This paper is based upon portions of a Ph.D. thesis by Calvin H. Long, Stanford University, 1964.

[3] C. Lewis and D. A. Skoog, *J. Am. Chem. Soc.*, **84**, 1101 (1962).

and it was suggested that the increase might be caused by a light-catalyzed air oxidation to give two moles of the species $I(SCN)_2^-$, which has absorption characteristics rather similar to I_2SCN^-.

We have now carried out further studies which have revealed that any of several oxidizing agents will cause enhancement of the ultraviolet absorption of iodine-containing solutions of thiocyanate ion and have demonstrated that the stoichiometry of these reactions is compatible with the following behavior of the iodine

$$I_2 + 4SCN^- \rightleftharpoons 2I(SCN)_2^- + 2e$$

This paper describes the evidence we have developed for this stoichiometry and also describes the properties and behavior of solutions of $I(SCN)_2^-$.

Experimental Section

Reagents and Solutions.—Sodium thiocyanate was recrystallized from reagent grade methanol until 5.0 g. of the material consumed less than 0.06 ml. of 0.01 *N* triiodide solution. Sodium perchlorate for adjusting ionic strengths of solutions was prepared by neutralization of reagent grade sodium hydroxide with 60% perchloric acid followed by evaporation. The other materials employed were reagent grade and used without further purification.

Solutions of sodium iodide and sodium thiocyanate were standardized periodically against silver nitrate. Standard potassium iodate solutions were prepared directly from the dried reagent grade salt. Hydrogen peroxide solutions were standardized by titration with a standard solution of quadrivalent cerium. Perchloric acid solutions were standardized with primary standard grade sodium carbonate. Iodine solutions were prepared by dissolving about 2 g. of finely ground iodine in 1 l. of dilute perchloric acid; the suspension was allowed to stand approximately 2 weeks before use. The resulting solution was nearly saturated and was found to be substantially free of triiodide ion, the concentration of the latter decreasing with aging.

The solutions used for final measurements were generally prepared by addition of the various reagents to small volumetric flasks cooled in an ice bath. Photochemical changes were avoided by surrounding the bath with a black cloth. Several minutes were required for temperature equilibration when these solutions were transferred to the cell compartment of the spectrophotometer; a constant value of absorbance was used as a criterion of temperature equilibrium.

Measurements.—The majority of the spectrophotometric measurements were made with a Beckman Model DU spectrophotometer, equipped with thermospacer attachments. The cell compartment was cooled by circulation of a refrigerated liquid from a thermostat bath; by surrounding the cell compartment with a layer of polystyrene foam insulation it was found possible to control cell temperatures to within ±0.1° over a range of 2 to 25°.

Calibrated 1-cm. silica cells were employed; for some measurements, solid silica spacers were used to reduce the path lengths to 0.1 cm.

Results

When acidic solutions of iodine and thiocyanate ion are aerated while exposed to sunlight, a rapid increase in the ultraviolet absorption maximum occurs; after approximately 1 hr. of photolysis the absorbance approaches a constant value which is somewhat greater than twice that of the original. These changes are illustrated in Figure 1. The absorption maximum for the photolyzed solution is at 302 mμ while that for the original is at 303 mμ. That the changes are a consequence of an air oxidation process is indicated by experiments in which solutions were photolyzed in the absence of oxygen; with these no absorption increase was found.

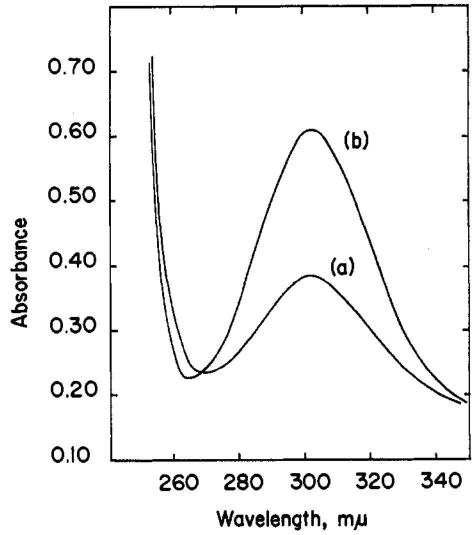

Figure 1.—Effect of photolysis on absorption spectra of iodine–thiocyanate solutions: (a) original solution; (b) after exposure to sunlight for 1 hr.

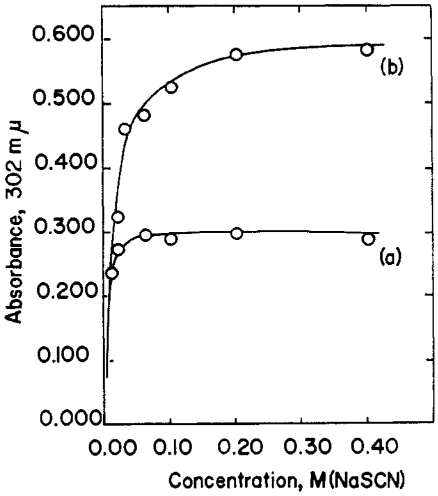

Figure 2.—Effect of thiocyanate concentration on unphotolyzed (a) and photolyzed (b) solutions of iodine and thiocyanate ion. Iodine concentration 6.1 × 10^{-5} *M*.

Figure 2 shows the effect of thiocyanate concentration on the photolyzed and unphotolyzed solutions. In the latter case, the absorbance values become constant at thiocyanate concentrations greater than about 0.05 *M*, presumably as a consequence of conversion of all of the iodine to the complex form. The large increases with photolysis in this region of thiocyanate concentration, then, must arise from a major alteration in the predominant components of the system. The work described below suggests that the observed changes result from occurrence of the reaction

$$O_2 + 2I_2 + 8SCN^- + 4H^+ \xrightarrow{h\nu} 4I(SCN)_2^- + 2H_2O$$

In the absence of light, changes similar to those shown in Figure 1 can be brought about with H_2O_2. The re-

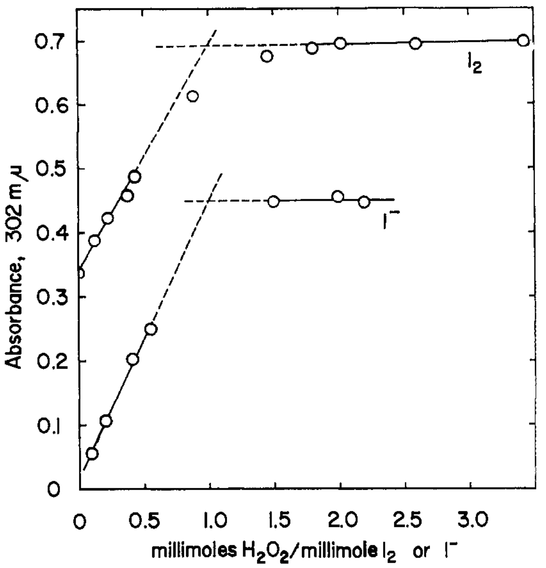

Figure 3.—Spectrophotometric titration curves for titration of iodine and of iodide ion in the presence of thiocyanate ion with a standard solution of hydrogen peroxide.

action is again slow, requiring 30–60 min. at 0° for completion as indicated by constant values for the absorbance.

To elucidate the stoichiometry of the peroxide reaction, spectrophotometric titrations of both iodide ion and of iodine in solutions of sodium thiocyanate were performed with standard solutions of hydrogen peroxide. Typical titration curves are shown in Figure 3. With either iodide ion or iodine an end point is observed at a mole ratio of reactants equal to unity. Reasonable equations for the reactions appear to be

$$H_2O_2 + I^- + 2SCN^- + 2H^+ \longrightarrow I(SCN)_2^- + 2H_2O$$

$$H_2O_2 + I_2 + 4SCN^- + 2H^+ \longrightarrow 2I(SCN)_2^- + 2H_2O$$

It was also found possible to obtain a potentiometric end point for these titrations employing a platinum–calomel electrode system. Stoichiometry identical with the above was indicated. It is of interest to note that under the conditions employed for these titrations, iodide ion is not oxidized by hydrogen peroxide to any significant extent in periods of up to 2 hr. if thiocyanate ion is absent.

Potassium iodate was also found to oxidize iodide ion or iodine dissolved in solutions of potassium thiocyanate, the products having an absorption spectrum identical with that formed with hydrogen peroxide or oxygen. With this reagent, however, the reactions were essentially instantaneous. A typical titration curve for iodide in the presence of thiocyanate ion is shown in Figure 4, curve b. The end point occurs at a mole ratio of iodate to iodide of 0.5; comparisons of the absorbance value in this instance with those for the peroxide titrations suggest that $I(SCN)_2^-$ is the product of both the oxidation of the iodide and the reduction of the iodate. The reaction, then, appears to be

$$6SCN^- + IO_3^- + 2I^- + 6H^+ \longrightarrow 3I(SCN)_2^- + 3H_2O$$

When solutions of iodine were titrated, the end point corresponded to

$$IO_3^- + 2I_2 + 10SCN^- + 6H^+ \longrightarrow 5I(SCN)_2^- + 3H_2O$$

It is noteworthy that in all of the titrations with iodate ion, the absorbance of the solutions continue to increase after the end point but at a lower rate than before. Furthermore, as shown by Figure 4a, blank solutions containing no iodide or iodine increased linearly in absorbance with concentration or added iodate. A spectral examination of the blank solutions showed an absorption peak identical with that obtained by oxidation of iodine-containing solutions, and it is reasonable to postulate that the following rapid reaction was occurring

$$IO_3^- + 6SCN^- + 6H^+ \longrightarrow I(SCN)_2^- + 2(SCN)_2 + 3H_2O$$

When an excess of iodide was added to the blank solutions immediately after titration, the absorbance values were found to increase by a factor of three, suggesting that the thiocyanogen formed in the initial reaction behaves as shown below.

$$(SCN)_2 + I^- \longrightarrow I(SCN)_2^-$$

If, however, iodide was introduced after the iodate–thiocyanate mixtures had stood for a few minutes, the increase in absorbance was appreciably less and was dependent upon the time of standing. Undoubtedly this decrease results from the slow hydrolysis of the thiocyanogen to give sulfate, hydrogen cyanide, and other products which do not react with iodine. Spectrophotometric titrations of iodate–thiocyanate mixtures with standard iodide solutions, if carried out rapidly, were found to yield end points at IO_3^- to I^- molar ratios of 0.5.

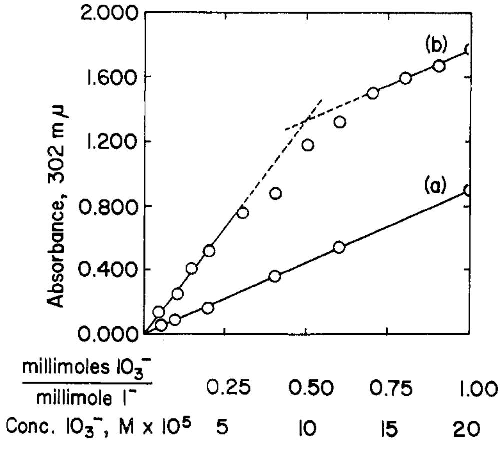

Figure 4.—Spectrophotometric titration curve for titration of iodide ion in the presence of thiocyanate ion with a standard solution of potassium iodate (b); blank titration (a).

Iodide ion and iodine in solutions of thiocyanate ion were also titrated with a standard solution of thiocyanogen. The latter was not very stable owing to hydrolysis of the thiocyanogen; the presence of thiocyanate ion in these solutions, however, inhibited the hydrolytic reaction sufficiently to make their use as standard reagents possible. End points in these titrations corresponded to the reaction

$$(SCN)_2 + I^- \longrightarrow I(SCN)_2^-$$

The absorption spectra of the mixtures were identical with those obtained with other oxidizing reagents.

Properties of $I(SCN)_2^-$ Solutions.—Solutions of $I(SCN)_2^-$ are conveniently prepared by adding a stoichiometric quantity of iodide to iodate ion dissolved in an acidic solution containing an excess of thiocyanate. At room temperature, such solutions tend to undergo irreversible decomposition, presumably forming sulfate and other oxidation products of the thiocyanate ion. The rate of the oxidation process is greatly reduced in the temperature range 0–10° particularly when the thiocyanate concentration is high (0.01–0.2 *M*), the ionic strength large (1.0–5.0 *M*), and the hydrogen ion concentration in the range 1.0–2.0 *M*. Such solutions are found to exhibit a decrease in absorbance of the $I(SCN)_2^-$ peak of less than 0.1%/hr. The factors affecting the decomposition of $I(SCN)_2^-$ solutions are similar to those found for the I_2SCN^- complex.[3]

The absorption maximum for $I(SCN)_2^-$ occurs at 302 mμ. The molar extinction coefficient for the complex at this wave length was estimated to be 44,500 ± 500 as determined from the absorbance of solutions containing an excess of thiocyanate ion, known concentrations of iodide or iodine, and an excess of hydrogen peroxide. A similar value was obtained from the slope of the titration curve shown in Figure 4a.

The Equilibrium $I(SCN)_2^- \rightleftharpoons I^- + (SCN)_2$.—When solutions of $I(SCN)_2^-$ were prepared by addition of exactly stoichiometric quantities of KIO_3 and KI to solutions containing an excess of thiocyanate ion, the absorbances at 302 mμ were found to be less than the theoretical values calculated from the molar extinction coefficient that was determined in the presence of an excess of oxidizing agent. Consideration of Figure 4b and the high reduction potential for KIO_3 suggested that the low absorbance data could not result from incomplete reduction of the KIO_3 but rather must be a consequence of equilibria giving products that absorb less than $I(SCN)_2^-$. Two equilibria that were suggested by analogy to the behavior of other halogen and pseudo-halogen species were

$$I(SCN)_2^- \rightleftharpoons I^- + (SCN)_2 \qquad (1)$$

$$I(SCN)_2^- \rightleftharpoons ISCN + SCN^- \qquad (2)$$

The data in Table I suggest that equilibrium 1 predominates in solutions stronger than 0.1 *M* in thiocyanate ion. It is seen that in such solutions, the absorbance values are independent of the concentration of thiocyanate ion, but that marked deviations from Beer's law occur. Further, the observed absorbances are appreciably lower than those calculated from the molar extinction coefficient for $I(SCN)_2^-$. Below 0.008 *M*, the absorbances become dependent upon the concentration of thiocyanate ion, suggesting that equilibrium 2 and perhaps others may also play a significant part in the solutions.

TABLE I

EVIDENCE FOR EQUILIBRIA 1 AND 2 IN SOLUTIONS OF $I(SCN)_2^-$

$I(SCN)_2^-$ concn., *M*	SCN^- concn., *M*	*A*/*l*, Exptl.	$\epsilon \times M_{I(SCN)_2^-}$, Calcd.
4.50×10^{-4}	0.40	17.93	19.80
	0.20	17.96	19.80
	0.10	17.95	19.80
4.50×10^{-5}	0.20	1.33	1.980
4.50×10^{-6}	0.20	0.092	0.198
4.50×10^{-4}	0.0080	11.04	19.80
	0.0040	7.43	19.80
	0.0020	5.24	19.80

TABLE II

EQUILIBRIUM QUOTIENT, K^a

$(M_{KIO_3} + 2M_{KI}) \times 10^5$	$(A/\epsilon l) \times 10^5$	$K \times 10^6$
0.450	0.207	2.86
	0.200	3.13
1.50	0.906	3.90
	0.827	5.49
	0.820	5.65
15.0	12.86	3.56
	13.35	4.52
45.0	40.46	5.08
	40.35	5.35[b]
	40.30	5.46[c]
	40.37	5.34[d]

[a] Temperature 6.6°; ionic strength = 1.2 *M*; SCN^- concentration 0.2 *M*. [b] Corrected for excess iodide (2.0×10^{-5} *M*). [c] Concentration of SCN^- 0.40 *M*. [d] Concentration of SCN^- 0.10 *M*.

TABLE III

VARIATIONS OF *K* WITH TEMPERATURE

Temp., °C.	No. of measurements	*K*	Std. dev. of measurements
1.0	6	2.02×10^{-6}	0.6×10^{-6}
4.0	3	5.15×10^{-6}	1.8×10^{-6}
6.6	11	4.6×10^{-6}	1.0×10^{-6}
9.0	3	9.50×10^{-6}	3.5×10^{-6}
12.0	3	11.03×10^{-6}	3.4×10^{-6}
25.0[a]	...	8×10^{-5}	

[a] Extrapolated value from plot of log *K* *vs.* 1/*T*.

Experiments were carried out to evaluate the equilibrium quotient for reaction 1. The data obtained are given in Table II. In these studies, $I(SCN)_2^-$ solutions of known concentrations were prepared by mixing carefully measured quantities of KIO_3 and KI in a 1:2 mole ratio. Decomposition of the $I(SCN)_2^-$ was prevented by maintaining a perchloric acid level of 1.0 *M* and by carrying out the preparations and measurements at 6.6°. The ionic strength was maintained at 1.2 *M* throughout. The value for the equilibrium quotient *K* was calculated as follows

$$K = \frac{[(SCN)_2][I^-]}{[I(SCN)_2^-]} = \frac{(M_{I(SCN)_2^-} - A/\epsilon l)^2}{A/\epsilon l}$$

This equation assumes that reaction 1 is the only significant equilibrium in the solution and that neither I^- nor $(SCN)_2$ absorbs appreciably at 302 mμ. The latter assumptions were verified by experiment.

The average value for the eleven measurements of *K* shown in Table II was found to be 4.6×10^{-6} with a standard deviation of 1.0×10^{-6}. It is probable that the two measurements made at the lowest $I(SCN)_2^-$ concentration (0.45×10^{-5} *M*) are significantly less 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.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF PADUA, PADUA, ITALY

Infrared Studies of Planar and Tetrahedral Inorganic Thiocyanates[1]

BY CESARE PECILE[2]

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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 $0.8\text{–}2.3 \times 10^4$ M^{-1} cm.$^{-2}$ for the thiocyanates and that of the isothiocyanates is in the range $9\text{–}12 \times 10^4$ 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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(2) Istituto di Chimica Fisica, Via Loredan 2, Padova, Italy.

(3) (a) A. Maki and J. C. Decius, *J. Chem. Phys.*, **31**, 772 (1959); (b) T. C. Waddington, *J. Chem. Soc.*, 2499 (1959); (c) W. Beck, *Chem. Ber.*, **95**, 341 (1962); (d) M. R. Petra and C. Curran, Abstracts, 141st National Meeting of the American Chemical Society, 1962; (e) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 262, 1286 (1965).

(4) L. H. Jones *J. Chem. Phys.*, **25**, 1069 (1956).

(5) M. M. Chamberlain and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 6412 (1959); M. E. Baldwin, *J. Chem. Soc.*, 471 (1961).

(6) C. Pecile, G. Giacometti, and A. Turco, *Atti Accad. Nazl. Lincei, Rend. Classe Sci. fis. mat. nat.*, **28**, 189 (1960).

(7) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

(8) A. Tramer, *J. Chim. Phys.*, **59**, 232, 241, 637 (1962).

(9) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(10) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).

(11) A. Turco, C. Pecile, and M. Nicolini, *J. Chem. Soc.*, 3008 (1962).

(12) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

(13) J. Chatt and L. A. Duncanson, *Nature*, **178**, 997 (1956); **181**, 43 (1958).

(14) E. Frasson, C. Panattoni, and A. Turco, *ibid.*, **199**, 803 (1963).

(15) A. C. Hazell, *J. Chem. Soc.*, 5745 (1963).

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