CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
UNIVERSITA' DI FIRENZE, FIRENZE, ITALY

Infrared Spectra between 100 and 2500 Cm.$^{-1}$ of Some Complex Metal Cyanates, Thiocyanates, and Selenocyanates

BY A. SABATINI AND I. BERTINI

Received January 18, 1965

The infrared spectra between 100 and 2500 cm.$^{-1}$ of a number of isocyanato, isothiocyanato, thiocyanato, and selenocyanato complexes have been recorded. The metal–nitrogen (or sulfur, or selenium) stretching vibrations have been assigned. The NCO group is shown to be N-coordinated in all compounds by comparison of the C–O stretching frequency in the coordinated and noncoordinated ligand. It is also found that the N–C–O, N–C–S, and N–C–Se bending frequencies have characteristic values depending on which atom is bonded to the metal ion.

Introduction

In complex ions of the formula $[M(NCX)_n]^{m-}$, where X is O, S, or Se and M a transition metal, it is of particular interest to obtain a reliable criterion to show whether the bonding to the central metal ion be through the nitrogen atom (N-, or iso series) or through the atom X (X-, or normal series). The infrared spectra of thiocyanato complexes, where X = S, have been extensively studied with this aim in view. Mitchell and Williams[1] found the C–N stretching frequency to be usually higher in S-thiocyanates than in N-thiocyanates, though there are some exceptions. The C–S stretching frequency, on the other hand, has been found to have the characteristic values of 780–860 cm.$^{-1}$ in N-thiocyanato complexes as opposed to *ca.* 700 cm.$^{-1}$ in S-thiocyanato complexes.[2–4] These assignments have been used to determine the structures of complexes of the type $[ML_2(NCS)_2]$, where M = Pd or Pt, which may be N- or S-bonded according to the substituent L.[3] The structures of various Mo(III) thiocyanato complexes were determined similarly.[4] Lewis, Nyholm, and Smith also found the N–C–S bending frequency in N-thiocyanato complexes to be very similar to the frequency in potassium thiocyanate, whereas it was lower and split into many components in S-thiocyanato complexes.

In the compounds $[(C_2H_5)_4N]_2[M(NCO)_4]$ where M = Mn, Co, Ni, Cu, or Zn, magnetic and spectroscopic measurements have shown that the compounds are N-cyanato and that the ligands are arranged tetrahedrally.[5] No infrared studies of these compounds have been reported.[5a]

Other fundamental vibrations which have not yet been studied are those which originate by the attachment of the ligand to the metal ion, namely the M–N (or M–X) stretching, M–N–C (or M–X–C) bending, and N–M–N (or X–M–X) bending vibrations. The present infrared measurements have been taken as far as 100 cm.$^{-1}$ in order to study these vibrational modes.

Experimental

The preparations of potassium salts[6] and cyanato complexes[5] have been described elsewhere. The procedures which follow were adopted for the other compounds. In each case stoichiometric quantities of reagents were employed.

$[(C_2H_5)_4N]_3[Cr(NCS)_6]$.—The following compounds were refluxed for 2 hr. in acetone: $(C_2H_5)_4NBr$, $CrCl_3 \cdot 6H_2O$, and KSCN. The compound, which crystallizes from acetone, is obtained by filtering the hot solution and cooling the filtrate.

Anal. Calcd.: C, 45.54; H, 7.64; N, 15.93. Found: C, 45.77; H, 7.52; N, 15.95.

$[(C_2H_5)_4N]_2[Co(NCS)_4]$.—Upon combination of aqueous solutions of $(C_2H_5)_4NCl$, $CoCl_2 \cdot 6H_2O$, and KSCN, the compound precipitated; it was subsequently recrystallized from absolute alcohol.

Anal. Calcd.: N, 15.23; NCS, 42.11. Found: N, 15.62; NCS, 42.30.

$[(C_2H_5)_4N]_2[Zn(NCS)_4]$.—Upon combination of aqueous solutions of $(C_2H_5)_4NCl$, $ZnCl_2$, and KSCN, the compound precipitated; it was subsequently recrystallized from absolute alcohol.

Anal. Calcd.: N, 15.06; NCS, 41.62. Found: N, 15.25; NCS, 41.52.

$[(C_2H_5)_4N]_4[Ni(NCS)_6]$.—The following compounds were heated in alcohol on a steam bath: $(C_2H_5)_4NBr$, $NiCl_2 \cdot 6H_2O$, and KSCN. The resulting mixture of solvent and precipitate was cooled and filtered. The filtrate was subjected to evaporation on a steam bath until the appearance of crystals. Cooling resulted in the formation of the compound which was further recrystallized from absolute alcohol.

Anal. Calcd.: N, 15.09; NCS, 37.54. Found: N, 15.30; NCS, 37.59.

$[(C_2H_5)_4N][Au(SCN)_4]$.—The compound precipitated upon mixing aqueous solutions of $AuCl_3$ and $(C_2H_5)_4NSCN$.

Anal. Calcd.: C, 25.76; H, 3.60; N, 12.52. Found: C, 25.81; H, 3.65; N, 12.27.

$[(C_2H_5)_4N]_2[Pd(SCN)_4]$.—Palladium(II) chloride was dissolved in concentrated HCl and dried. Absolute alcohol was added and the mixture was refluxed with $(C_2H_5)_4NCl$ and KSCN for 1 hr. The solution was then filtered and evaporated to a small volume. Acetone was added to the hot solution, followed by the addition of chloroform until a light turbidity appeared. Upon cooling the solution, the compound precipitated; it was repeatedly recrystallized from acetone and chloroform.

---

(1) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

(2) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959).

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

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

(5) D. Forster and D. M. L. Goodgame, *ibid.*. 2790 (1964).

(5a) NOTE ADDED IN PROOF.—After this article had been submitted, the paper by D. Forster and D. M. L. Goodgame, *ibid.*, 262 (1965), appeared. Our results are in good agreement with those presented in the above work.

(6) A. Rosenheim and R. Cohn, *Z. anorg. allgem. Chem.*, **27**, 285, 289 (1901); P. Walden, *ibid.*, **23**, 374 (1900); W. Peters, *ibid.*, **77**, 182 (1912); I. Bellucci, *Gazz. chim. ital.*, **35I**, 346(1905); P. T. Cleve, *J. prakt. Chem.*, **94**, 14, 18 (1865); G. B. Buckton, *Liebigs Ann. Chem.*, **92**, 281, 286 (1854); *cf.* Gmelin, "Handbuch der Anorganischen Chemie," Platin, Teil C, Verlag Chemie, Berlin, 1953, p. 210.

Anal. Calcd.: C, 40.09; H, 6.73; N, 14.03. Found: C, 40.21; H, 6.84; N, 14.48.

$[(C_2H_5)_4N]_2[Pt(SCN)_6]$.—Potassium hexathiocyanatoplatinate(IV) was heated in alcohol with $(C_2H_5)_4NCl$. From the filtrate the compound was obtained after cooling; it was recrystallized from alcohol.

Anal. Calcd.: C, 32.86; H, 5.01; N, 13.94. Found: C, 32.92; H, 5.10; N, 13.96.

$[(CH_3)_4N]_2[Pt(SeCN)_6]$.—Potassium hexaselenocyanatoplatinate(IV) and $(CH_3)_4NCl$ were heated in alcohol at 70°. Upon filtering, the compound separated from the filtrate after cooling; it was recrystallized from alcohol at 70°.

Anal. Calcd.: C, 17.28; H, 2.49; N, 11.51. Found: C, 17.59; H, 2.54; N, 11.68.

$[(C_2H_5)_4N]_2[Pt(SeCN)_6]$.—This compound was obtained in a manner similar to that used in the preparation of the preceding one. Instead of $(CH_3)_4NCl$, $(C_2H_5)_4NCl$ was substituted.

Anal. Calcd.: C, 24.34; H, 3.71; N, 10.32. Found: C, 24.71; H, 3.83; N, 10.55.

$Cs_2[Pt(SeCN)_6]$.—Tetraethylammonium hexaselenocyanatoplatinate(IV) was dissolved in alcohol and solid CsI was added. After the mixture was stirred for 30 min., the compound was filtered out and recrystallized from alcohol at 70°.

Anal. Calcd.: N, 7.71. Found: N, 7.88.

The infrared spectra were recorded on Perkin-Elmer Model 421 (2500–600 cm.$^{-1}$), Model 21 with a CsBr prism (650–380 cm.$^{-1}$), and Model 301 (400–100 cm.$^{-1}$) spectrophotometers, all using Nujol mulls.

Results and Discussion

The frequencies of the fundamental vibrations of the complex ions studied are given in Table I. Where the C–N stretch in cyanato complexes is diffuse, or shows minor maxima or shoulders, only the frequency of the main peak is reported. The assignments of the absorption bands due to the C–N stretching, C–X stretching, and N–C–X deformation are easily made by comparing the spectra of the complexes with those of the simple salts, KNCX. Those bands which cannot occur in the free ligand, namely the M–N (M–X) stretching and M–N–C (M–X–C) and N–M–N (X–M–X) bending modes, are expected to occur in the far-infrared region, with the M–N (M–X) stretch at the highest frequency. As no predictions can be made concerning the deformational modes which are expected at low frequencies, these have not been assigned. Furthermore, lattice vibrations may be expected to occur with frequencies around 100 cm.$^{-1}$.

The spectra of the potassium salts are generally more complicated than those of the corresponding tetraethylammonium salts, in that many bands appear to be split into more than one component. Analogous effects have

TABLE I

INFRARED ABSORPTION FREQUENCIES (CM.$^{-1}$) OF ISOCYANATO, ISOTHIOCYANATO, THIOCYANATO, AND SELENOCYANATO COMPLEXES[a]

Compound	C–N str.	C–O, C–S, or C–Se str.	N–C–O, N–C–S, or N–C–Se bend.	M–N, M–S, or M–Se str.	
$[(C_2H_5)_4N]_2[Mn(NCO)_4]$	2170 s, b	1328 m	626 m	333 s	159 m
$[(C_2H_5)_4N]_2[Co(NCO)_4]$	2183 s, b	1329 m	620 m	349 s	183 m
$[(C_2H_5)_4N]_2[Ni(NCO)_4]$	2196 s, b	1330 m	621 m	344 s	160 w, b
$[(C_2H_5)_4N]_2[Cu(NCO)_4]$	2200 s, b	1324 m	618 m	339 ms	231 vw, 215 mw, 162 mw
$[(C_2H_5)_4N]_2[Zn(NCO)_4]$	2200 s, b	1333 m	624 m, 615 m	328 m	178 m
$[(C_2H_5)_4N]_3[Cr(NCS)_6]$	2078 s		483 m	364 s	
$[(C_2H_5)_4N]_2[Co(NCS)_4]$	2065 s	844 w, 838 sh	481 w	311 vs	176 m
$K_2[Co(NCS)_4]\cdot 4H_2O$	2085 sh, 2067 s	820 vw	478 w, b	286 mw, b	187 w, b
$[(C_2H_5)_4N]_4[Ni(NCS)_6]$	2112 sh, 2103 s	828 vw	470 m	240 m	
$[(C_2H_5)_4N]_2[Zn(NCS)_4]$	2072 s	837 vw	482 m	287 s	169 ms
$K_2[Zn(NCS)_4]\cdot 4H_2O$	2097 s, 2065 s	820 w	474 w, b	253 w, b	174 w, b
$[(C_2H_5)_4N]_2[Pd(SCN)_4]$	2112 sh, 2109 s, sp	698 w, 694 sh	465 w, 433 sh, 429 m, 418 w	294 m	170 m, 132 vw, 107 m
$K_2[Pd(SCN)_4]$	2122 s, 2093 s	709 sh, 703 w, 697 sh	474 vw, 468 vw, 442 w, 432 w	300 w, 286 m	194 m, 172 m, 146 m, 127 m
$K_2[Pt(SCN)_4]$	2130 s, 2100 s, 2052 vw	697 w	478 vw, 472 vw, 438 m, 427 m, 419 sh	293 w, 283 m	196 m, 179 m, 150 m. 139 m, 123 m, 109 m
$[(C_2H_5)_4N][Au(SCN)_4]$	2127 s, sp	695 vw	454 m, 415 m	314 mw, 292 m	170 m, 147 mw, 105 mw
$K[Au(SCN)_4]$	2140 sh, 2133 s, sp 2080 vw	700 w	462 vw, 457 vw, 414 mw	308 w, 294 m	181 m, 142 mw
$K_2[Hg(SCN)_4]$	2135 s, 2127 s, 2108 m, 2090 sh, 2056 w	719 w, 713 vw, 706 vw	463 m, 452 w, 434 m, 421 w	285 m, 255 w	166 s, 124 vs
$[(C_2H_5)_4N]_2[Pt(SCN)_6]$	2120 s, sp	692 w	461 vw, 457 vw, 418 w, 415 w	283 ms	185 m, 163 sh, 156 vw, 121 m
$K_2[Pt(SCN)_6]$	2130 s, sp	699 sh, 695 w, 688 vw	462 vw, 433 sh, 427 w, 418 m	291 mw, 281 m	191 ms, 154 m, 131 mw
$[(C_2H_5)_4N]_2[Pt(SeCN)_6]$	2133 sh, 2127 s, sp	524 m	418 w, 397 vw, 371 m, 365 m	219 sh, 212 m	130 s
$[(CH_3)_4N]_2[Pt(SeCN)_6]$	2123 s, sp	528 m	398 vw, 373 m	218 w, 210 w	132 ms, 117 m
$Cs_2[Pt(SeCN)_6]$	2132 s, sp	522 m	387 w, 376 w, 363 m	219 mw, 203 mw	150 m, 111 m
$K_2[Pt(SeCN)_6]$	2130 s, sp	519 m	390 w, 379 m, 367 m	222 w, 207 w	160 s, 125 s, 112 s, 100 s

[a] s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder; sp, sharp.

often been noted with other compounds; that is, the tetraethylammonium salt gives the simplest spectrum. This implies that interactions, electrostatic or otherwise, with the larger cation are relatively smaller.

The M–N stretching frequencies of the cyanato complexes vary in the same way as the stabilities of other tetrahedral complexes of the divalent first row transition elements, *i.e.*, Mn < Co > Ni > Cu > Zn. Distortions from the true tetrahedral configuration are known to exist in the ions $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$, and they cause a splitting of the degenerate M–X stretching and X–M–X deformation modes.[7] The compound $[(C_2H_5)_4N]_2[Cu(NCO)_4]$ shows a single M–N stretching band but the band at lower frequencies is split. Thus, while the infrared spectrum does not unambigously indicate the ion $[Cu(NCO)_4]^{2-}$ to be distorted from the regular tetrahedral configuration, the considerable splitting of the low-frequency band does support such a hypothesis. It is worth noting also that the low-frequency band in the nickel cyanato complex is weak and very diffuse.

The M–N stretching frequency in N-thiocyanato complexes is a little lower than in the corresponding cyanato complexes. It is much lower, though clearly still in the same order, than the M–N stretching frequency in the corresponding ammine complex—compare the values of 364, 287, and 240 cm.$^{-1}$ for the thiocyanato complexes $[Cr(NCS)_6]^{3-}$, $[Zn(NCS)_4]^{2-}$, and $[Ni(NCS)_6]^{4-}$ with the values for the complexes where ammonia has replaced the thiocyanate ions, 470, 437, and 334 cm.$^{-1}$.[8,9]

Turning to the S-thiocyanato complexes, the M–S stretch gives a single band at *ca.* 290 cm.$^{-1}$ in both $[(C_2H_5)_4N]_2[Pd(SCN)_4]$ and $[(C_2H_5)_4N]_2[Pt(SCN)_6]$, but gold gives a split band at *ca.* 310 and 290 cm.$^{-1}$ in both $K[Au(SCN)_4]$ and $[(C_2H_5)_4N][Au(SCN)_4]$.

X-Ray powder photographs show $K_2[Pt(SeCN)_6]$ to be isomorphous with $K_2[Pt(SCN)_6]$, which shows that selenium is the coordinating atom. The band at 212 cm.$^{-1}$ is therefore assigned as the Pt–Se stretching frequency.

The behavior of the N–C–S bending vibration is very interesting. In the spectrum of solid KSCN bands at 484 and 470 cm.$^{-1}$ are observed and the splitting is due to the site symmetry of the NCS^- ion in the crystal.[10] In N-thiocyanato complexes one band is found around 475 cm.$^{-1}$, a value very similar to that of the uncoordinated ion. In S-thiocyanato complexes more than one band is observed, in the range 400–480 cm.$^{-1}$, the most intense band lying around 420 cm.$^{-1}$. It thus appears that the bonding in thiocyanato complexes may be characterized by examining the N–C–S bending frequencies: N-bonded groups absorb at *ca.* 475 cm.$^{-1}$, while S-bonded groups absorb at lower frequencies. The most intense band is in the region of 420 cm.$^{-1}$. This criterion may be used to advantage when there are absorption bands in the region 700–850 cm.$^{-1}$ which can mask the weak C–S stretching band. The S-bonded complexes discussed here contain more than one NCS group. It may be observed also that the N–C–S bending mode gives rise to more than one absorption band. The hypothesis that the M–S–C bonds are always nonlinear[4] explains the multiplicity of the S–C–N bending frequencies, since the ion no longer has a regular configuration.

The C–S stretching frequency is higher in M–NCS-type complexes than in M–SCN-type complexes. This has been explained on the basis of the correspondingly greater double bond character of the C–S bond in M–NCS than in M–SCN.[2,4] The same argument may be used to explain the higher frequency of the N–C–S bending mode.

The bending modes in cyanato and selenocyanato complexes show a similar behavior with respect to the donor atom. A single N–C–O bending band is observed in the N-bonded cyanato complexes, at *ca.* 620 cm.$^{-1}$, as compared with bands at 637 and 628 cm.$^{-1}$ in KNCO.[11] On the other hand, in the Se-bonded selenocyanato complex of Pt(IV) a group of bands is found, the most intense of which is at *ca.* 370 cm.$^{-1}$. These must arise from the Se–C–N bending mode and their frequency is considerably less than the Se–C–N bending frequencies in KSeCN—424 and 416 cm.$^{-1}$.[12–14]

Fermi resonance occurs between the overtone of the bending and the fundamental C–O stretching frequencies in KNCO.[11] This gives rise to a doublet at 1207 and 1301 cm.$^{-1}$. The unperturbed C–O stretching vibration should have a value of 1254 cm.$^{-1}$. In the cyanato complexes the C–O stretching is shifted to *ca.* 1330 cm.$^{-1}$ and the resonance with the bending overtone disappears. The shift of this band indicates N bonding and supports the conclusion of Forster and Goodgame that these complexes are all N-bonded.[5] For the selenocyanato complex, however, the C–Se stretching frequency of 524 cm.$^{-1}$ in the complex is less than the frequency of 558 cm.$^{-1}$ in KSeCN.[12] This is further evidence that the bonding occurs through the selenium atom.

The absorption band associated with the C–N stretching mode in the cyanato complexes is very diffuse and the frequency, just as in the N- and S-thiocyanato complexes and the selenocyanato complex, is higher than in the potassium salt. The C–N stretching band does not vary sufficiently to characterize the coordination type in thiocyanato complexes, though it is often sharper and of higher frequency in the S-bonded complexes. This has already been discussed by others.[2–4]

Acknowledgment.—The authors thank Professor L. Sacconi for having suggested this problem and for helpful discussion. Thanks are expressed to the Italian "Consiglio Nazionale delle Ricerche" for financial support.

---

(7) A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

(8) J. M. Terrasse, H. Poulet, and J. P. Mathieu, *Spectrochim. Acta*, **20**, 305 (1964).

(9) L. Sacconi, A. Sabatini, and P. Gans, *Inorg. Chem.*, **3**, 1772 (1964).

(10) L. J. Jones, *J. Chem. Phys.*, **28**, 1234 (1958).

(11) A. Maki and J. C. Decius, *ibid.*, **31**, 772 (1959).

(12) H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 368 (1960).

(13) A. Turco, C. Pecile, and M. Niccolini, *Proc. Chem. Soc.*, 213 (1961).

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