225. *Vibrational Spectra of Pseudo-halide Complexes. Part II.*[1] *Planar and Octahedral Isocyanate Complexes.*

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The preparations of $(Me_4N)_2Sn(NCO)_6$ and $(Me_4N)_2Pd(NCO)_4$ are described. Infrared spectral studies show that both complexes contain *N*-bonded cyanate groups. The solution spectrum of the tin(IV) compound is in accord with O_h symmetry for the anion, indicating that there is no pronounced departure from linearity of the Sn–NCO groups under these conditions. The solution spectrum of the palladium(II) complex is also relatively simple, but the solid-state spectra of both compounds are more complicated.

Recently we described [2] the preparation of a series of complexes containing the tetrahedral anions $M(NCO)_4^{2-}$. Subsequently, we examined the overall symmetries of these anions, and also of the $Fe(NCO)_4^-$ ion, by means of infrared spectroscopy.[1] It seemed desirable to obtain similar information for isocyanato-complex ions of basically octahedral or planar structure. Accordingly, we have prepared the tetramethylammonium salts of the $Sn(NCO)_6^{2-}$ and $Pd(NCO)_4^{2-}$ anions, by the exchange method outlined previously,[2] and report here the results of infrared spectral studies on these compounds.

Tetramethylammonium Hexaisocyanatostannate(IV).—This compound appears to be the first cyanato- or isocyanato-complex of tin, although several unsuccessful attempts to prepare tin(IV) isocyanate have been reported.[3] The compound $(Me_4N)_2[Sn(NCO)_6]$ is stable in air but is hydrolysed readily by water.

There are two structural problems concerning the $Sn(NCO)_6^{2-}$ ion about which examination of the infrared spectra can provide useful information. The first of these is whether the NCO groups are co-ordinated to the central metal ion through nitrogen or through oxygen. There are no proven examples of compounds containing cyanate groups co-ordinated to metal ions via oxygen, but aryl cyanates have recently been described.[4] Both thiocyanato- and isothiocyanato-complexes are well known. With these compounds the question of bonding (*i.e.*, M–N or M–S) can usually be finally settled by means of a full *X*-ray structural determination. In the case of compounds involving NCO groups, however, distinction between cyanato- or isocyanato-complexes by *X*-ray methods would be more difficult, and therefore studies of the vibrational spectra assume greater importance. The second problem is the determination of the overall symmetry of the anion, since even

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[1] Part I, D. Forster and D. M. L. Goodgame, *J.*, 1965, 262.
[2] D. Forster and D. M. L. Goodgame, *J.*, 1964, 2790.
[3] F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 1961, **17**, 977.
[4] R. Stroh and H. Gerber, *Angew. Chem.*, 1960, **72**, 1000; D. Martin, *ibid.*, 1964, **76**, 303.

if the co-ordination polyhedron around the tin atom has O_h symmetry the Sn–NCO groups may be bent.

The infrared spectrum of the compound $(Me_4N)_2Sn(NCO)_6$ has been examined, as a Nujol mull, in the region 4000—140 cm.$^{-1}$, and in solution over a more limited range (see below). The results are shown in Table 1.

The three fundamental vibrational modes of the cyanate ion have the following frequencies in potassium cyanate:[5] ν_1 (C–N stretch) 2165 cm.$^{-1}$, ν_2 (doubly degenerate NCO bend) 637, 628 cm.$^{-1}$, and ν_3 (C–O stretch) 1207 cm.$^{-1}$. The infrared-active and -inactive modes of a species of the type $M(NCO)_6$ with O_h symmetry are listed in Table 2 (the Raman-active modes, ν_1—ν_{11}, have been omitted). The modes ν_{12} and ν_{13} of $M(NCO)_6$ are closely related to ν_1 and ν_3, respectively, of NCO^- and are, effectively, the C–N and C–O stretches of the co-ordinated cyanate groups. Deformation A, ν_{15}, of $M(NCO)_6$ is likewise related to ν_2 of NCO^-.

The solution spectrum of $(Me_4N)_2Sn(NCO)_6$ shows two bands, at 2183 and 622 cm.$^{-1}$, assignable as fundamentals. The weak band at 3534 cm.$^{-1}$ is most probably a combination band. The very strong band at 2183 cm.$^{-1}$ may be assigned as ν_{12}, the C–N stretch, and the band at 622 cm.$^{-1}$ as ν_{15}. We were unable to obtain a solution spectrum of the compound in the region where ν_{13} would be expected, because no suitable solvent could be found. The compound was either insoluble in or was decomposed by the solvents which do not absorb in this region. However, in the mull spectrum the C–O stretch, ν_{13}, was observed as a weak band at 1307 cm.$^{-1}$. This value for ν_{13} indicates that the cyanate groups in the $Sn(NCO)_6^{2-}$ anion are co-ordinated via nitrogen, since ν_{13} for a cyanato-complex would be

TABLE 1.

Infrared data (cm.$^{-1}$) for the complexes.

$(Me_4N)_2Sn(NCO)_6$		
Mull	Soln.	Assignment
3546w	3534w †	Combination
2270sh 2188vs	2183vvs ‡	ν_{12}
1307vw	§	ν_{13}
667sh 622s, br	622s ‡	ν_{15}
383vs	—	ν_{14}
235s 216s	—	ν_{16} and/or ν_{17} [a]

$(Me_4N)_2Pd(NCO)_4$		
Mull	Soln.	Assignment *
	3623w †	Combination
3497w	3496w †	Combination
2190—2200v.br, s	2203vvs ‡	ν_{20}
1319m	§	ν_{21}
637vw		?
613m 604m	614s ‡	ν_{23}
594s	595s ‡	ν_6
408sh 384s 350sh	—	ν_{22}
274vw	—	?

* For D_{4h} model. † In nitromethane. ‡ In acetone. § No suitable solvent for this region. [a] See text.

TABLE 2.

Inactive and infrared-active vibrations of $M(NCO)_6$, O_h symmetry.

Description	No.	Designation	Activity	Description	No.	Designation	Activity
C–N stretch, out-of-phase	ν_{12}	T_{1u}	Active	$M–N_6$ deformation	ν_{17}	T_{1u}	Active
C–O stretch, out-of-phase	ν_{13}	T_{1u}		M–NCO deformation A	ν_{18}	T_{2u}	Inactive
$M–N_6$ degenerate stretch	ν_{14}	T_{1u}		M–NCO deformation B	ν_{19}	T_{2u}	
M–NCO deformation A *	ν_{15}	T_{1u}		M–NCO deformation C ‡	ν_{20}	T_{2u}	
M–NCO deformation B †	ν_{16}	T_{1u}					

* Deformation A may be represented by $\underset{\downarrow}{M}-\overset{\uparrow}{N}-\underset{\downarrow}{C}-\overset{\uparrow}{O}$. † Deformation B may be represented by $\overset{\uparrow}{M}-\underset{\downarrow}{N}-\underset{\downarrow}{C}-\overset{\uparrow}{O}$. ‡ Deformation C may be represented by $M-\overset{\uparrow}{N}-\overset{\uparrow}{C}-\overset{\uparrow}{O}$.

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[5] A. Maki and J. C. Decius, *J. Chem. Phys.*, 1959, **31**, 772.

expected [3] to lie below the frequency (1207 cm.$^{-1}$) of the C–O stretch of the free NCO^- ion. This is analogous to the distinction between *N*- and *S*-bonded thiocyanate groups from the values of the C–S stretching frequencies.[6]

The solution spectrum shows that, under these conditions, the $Sn(NCO)_6^{2-}$ ion has a high degree of symmetry. Of the possible models for this anion involving bent Sn–NCO groups that with the highest symmetry belongs to point group S_6. Both T_{1u} and T_{2u} in O_h transform as $A_u + E_u$ in S_6, and both A_u and E_u modes are infrared-active. Thus any departure of $Sn(NCO)_6^{2-}$ from O_h symmetry will be manifest in a splitting of ν_{12}—ν_{17} and the appearance of new bands originating from those modes, ν_{18}—ν_{20}, which are inactive in O_h symmetry. Although the solution data were limited to only two bands, ν_{12} and ν_{15}, neither of these showed any splitting. It can be concluded from this that, in solution at any rate, the symmetry of the $Sn(NCO)_6^{2-}$ ion approaches quite closely to O_h, and that there is little or no bending of the Sn–NCO groups.

The spectrum of the solid compound is more complex. Thus, ν_{12} and ν_{15} are broader than in the solution spectrum and each of these bands has a shoulder to higher energy. This may be due either to the fact that the site symmetry of the complex anion in the solid state is lower than O_h, or to distortion of individual anions.

The solid state spectrum from 400 to 140 cm.$^{-1}$ shows three strong bands, at 383, 235, and 216 cm.$^{-1}$. It was found [1,3] for the tetrahedral species $Si(NCO)_4$ and $M(NCO)_4^{n-}$ that the $M–N_4$ degenerate stretch was at higher energy than the $M–Cl_4$ degenerate stretch, ν_3, for the analogous, tetrahedral chloro-complexes. For example, the values for $Si(NCO)_4$ and $SiCl_4$ are 727 cm.$^{-1}$ [3] and 608 cm.$^{-1}$,[7] respectively, while those for the tetraethylammonium salts of $Co(NCO)_4^{2-}$ and $CoCl_4^{2-}$ are 345 cm.$^{-1}$ [1] and ~300 cm.$^{-1}$,[8] respectively. Since the infrared-active Sn–Cl stretch (ν_3) for the $SnCl_6^{2-}$ ion is reported [9] to be at 294 cm.$^{-1}$, the ν_{14} band for the $Sn(NCO)_6^{2-}$ ion would be expected to lie above 300 cm.$^{-1}$. We assign the strong band at 383 cm.$^{-1}$ in the spectrum of $(Me_4N)_2Sn(NCO)_6$ as ν_{14}.

Assignment of the strong bands at 216 and 235 cm.$^{-1}$ is not straightforward, as they could arise from either or both of the two deformation modes ν_{16} and ν_{17}. Since these bands were observed in the solid state and, as mentioned above, splittings were found for some of the higher energy bands under these conditions, it is possible that they are both components of either ν_{16} or ν_{17}, as these are triply degenerate in O_h symmetry. Certainly one would expect ν_{17} to occur in this region, since the bands due to the T_{1u} bending mode, ν_4, of heavy metal MCl_6^{2-} ions are found in the range 170—200 cm.$^{-1}$.[10] But whether both the 216 and 235 cm.$^{-1}$ bands are due to ν_{17}, or whether ν_{16} occurs in the same region, remains uncertain.

Bistetramethylammonium Tetraisocyanatopalladate(II).—To our knowledge, no simple or complex cyanates of palladium have been described previously. This compound resembles the other anionic isocyanate complexes with large, quaternary cations in being quite soluble in polar organic solvents such as nitromethane, nitrobenzene, or acetone, but insoluble in or decomposed by hydroxylic solvents.

Since the cyanate group appears to have little or no tendency to act as a bridging ligand, and six-co-ordinate complexes of palladium(II) are relatively rare, it can be assumed with a fair degree of certainty that the $Pd(NCO)_4^{2-}$ anion has a planar structure.

The fundamental vibrations for $M(NCO)_4$ species with D_{4h} symmetry have been given by Miller and Carlson,[3] and the infrared-active modes are listed in Table 3. On the D_{4h} model, the very strong band at 2203 cm.$^{-1}$ in the solution spectrum may be assigned as ν_{20}. As in the case of $(Me_4N)_2Sn(NCO)_6$, we were unable to obtain a solution spectrum in the

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[6] J. Lewis, R. S. Nyholm, and P. W. Smith, *J.*, 1961, 4590.

[7] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, 1963.

[8] R. J. H. Clark and T. M. Dunn, *J.*, 1963, 1198; A. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, 1964, **86**, 17.

[9] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J.*, 1963, 2189.

[10] D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, 1963, **19**, 925.

TABLE 3.

Infrared-active vibrations of $M(NCO)_4$, D_{4h} symmetry.*

Description †	No.	Design.	Description †	No.	Design.
M–NCO deformation A, out-of-plane	ν_6	A_{2u}	M–N stretch	ν_{22}	E_u
M–NCO deformation B, out-of-plane	ν_7	A_{2u}	M–NCO deformation A, in-plane	ν_{23}	E_u
M–NCO deformation C, out-of-plane	ν_8	A_{2u}	M–NCO deformation B, in-plane	ν_{24}	E_u
C–N stretch, out-of-phase	ν_{20}	E_u	M–NCO deformation C, in-plane	ν_{25}	E_u
C–O stretch, out-of-phase	ν_{21}	E_u			

* From ref. 3. † See foot of Table 2 for representations of deformations A, B, and C.

region of the C–O stretch. However, in the solid state this band was found at 1319 cm.$^{-1}$, which value is in accord with the proposed formulation as an isocyanato-complex.

The bands at 614 and 595 cm.$^{-1}$ are assigned as ν_{23} and ν_6 respectively, the in-plane and out-of-plane deformation A modes. This provides good evidence for the square-planar distribution of the Pd–N bonds. A $Pd–N_4$ structure based on a distorted tetrahedron would also give rise to two deformation A modes, but would give two C–N stretches [as found [1] for the distorted tetrahedral (D_{2d}) anion $Cu(NCO)_4^{2-}$].

The fact that there are only four bands assignable as fundamentals above 450 cm.$^{-1}$ does not allow any decision to be made concerning the linearity of the Pd–NCO groups, since a C_{4h} model (involving bent Pd–NCO groups) has the same number of infrared-active fundamentals as the D_{4h} model.

The solid-state spectrum of the compound is more complex than that obtained for solutions. The band due to ν_{20} becomes much broader and a pronounced splitting is observed for ν_{23}. In the far-infrared region a broad, strong band is found at 384 cm.$^{-1}$ with shoulders at 408 and 350 cm.$^{-1}$. This broad absorption can be assigned to ν_{22}, the Pd–N stretch. However, since the ν_{22} mode is doubly degenerate in D_{4h}, only two components would have been expected if the anions either are distorted or occupy lattice sites of symmetry lower than D_{4h}. The extra complexity of this band at ~380 cm.$^{-1}$ may arise from coupling with lattice vibrations.

A very weak band was observed at 274 cm.$^{-1}$ but the low intensity makes it unlikely that it arises from a fundamental mode. No other bands were observed down to 200 cm.$^{-1}$ and it appears that the remaining deformation modes lie below this frequency.

EXPERIMENTAL

Preparation of the Compounds.—*Tetramethylammonium tetraisocyanatopalladate*(II). Tetramethylammonium tetrachloropalladate(II) (2·0 g.) was shaken for 1 hr. in acetone (20 ml.) with silver cyanate (~3·5 g.). The resulting pale orange solution was filtered and then evaporated to dryness *in vacuo*, orange crystals remaining. The *complex* was freed from any traces of silver salts by redissolving it in acetone, filtering the solution, and then removing the solvent *in vacuo* (80% yield, m. p. 129°) (Found: C, 33·5; H, 5·8; N, 19·6; Pd, 24·5. $C_{12}H_{24}N_6O_4Pd$ requires C, 34·1; H, 5·7; N, 19·9; Pd, 25·2%).

Tetramethylammonium hexaisocyanatostannate(IV). Tetramethylammonium hexachlorostannate(IV) (2·0 g.) was shaken for 1 hr. in acetone (20 ml.) with silver cyanate (~4·5 g.). The mixture was then filtered and the filtrate added to diethyl ether. The resulting white *complex* was purified by dissolving it in acetone, filtering the solution and reprecipitating the complex by addition of diethyl ether (74% yield). The compound does not melt below 350° (Found: C, 31·9; H, 4·7; N, 21·4. $C_{14}H_{24}N_8O_6Sn$ requires C, 32·4; H, 4·7; N, 21·6%).

Infrared Spectra.—These were obtained as described previously.[1] The compounds $(Me_4N)_2(MCl_4)$, M = Fe(II) or Cu(II), were used to identify absorption bands due to the tetramethylammonium ion. Cation absorption interfered in the region 1400—1300 cm.$^{-1}$.

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