40. *Vibrational Spectra of Pseudohalide Complexes. Part I. Tetrahedral Isocyanate Complexes.*

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Infrared spectra of the $[M(NCO)_4]^{2-}$ ions, where M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and of the $[Fe^{III}(NCO)_4]^-$ ion, were studied. The solution spectra of all of the ions, except the copper(II) complex, can be satisfactorily interpreted with a T_d model (*i.e.*, linear M–NCO groupings). The spectrum of $[Cu(NCO)_4]^{2-}$ is more complicated than are those of the other ions, and is consistent with D_{2d} symmetry. The lowering of symmetry in this case is probably caused by distortion of the $Cu-N_4$ tetrahedron rather than by kinking of the Cu–NCO groups.

WE have described[1] the preparation of the compounds $(Et_4N)_2[M(NCO)_4]$, where M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, and also the results of magnetic, electronic spectral, and *X*-ray diffraction studies on the complexes. The preparation of the analogous iron(II) complex, and details of its electronic spectrum, will be reported later.

These studies have shown that the environment of the metal ion in the $[M(NCO)_4]^{2-}$ species is that of a fairly regular tetrahedron, except in the case of the copper(II) complex where the tetrahedron was apparently distorted. However, the use of magnetic and electronic spectral properties does not necessarily permit decisions to be made concerning the overall symmetry of molecules, since the metal ion electronic energy levels may be relatively insensitive to changes in symmetry beyond the first co-ordination sphere. Thus it was not possible to decide whether or not the $[M(NCO)_4]^{2-}$ ions had overall T_d symmetry. A study of the vibrational spectra was therefore undertaken to obtain more information about the symmetry of these ions. Although there have been numerous reports[2] concerning the infrared spectra of transition metal " thiocyanato " complexes, no studies of transition-metal isocyanato-complexes appear to have been described.

The infrared spectra of the isocyanato-complex anions have been examined in the region 4000—200 cm.$^{-1}$. In addition a nitromethane solution of tetraethylammonium tetraisocyanatozincate(II), solid potassium tetraisocyanatocobaltate(II) and solid n-butyltriphenylphosphonium tetraisocyanatocobaltate(II) have been studied below 200 cm.$^{-1}$. The results are in Table 1. An attempt to obtain a Raman spectrum of the $[Zn(NCO)_4]^{2-}$ ion in nitromethane was rather unsuccessful in that only one band was observed (at 2250 cm.$^{-1}$). The 2M-solution scattered very weakly.

The ions have infrared absorption bands, assignable as fundamentals, in the following regions: ~2200, ~1330, ~620, 410—290, and ~185 cm.$^{-1}$. The detailed work of Miller

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[1] Forster and Goodgame, *J.*, 1964, 2790.

[2] Lewis, Nyholm, and Smith, *J.*, 1961, 4590; Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412; Turco and Pecile, *Nature*, 1961, **191**, 66.

and Carlson[3] on the vibrational spectra of silicon tetraisocyanate and germanium tetraisocyanate has been of great value in assigning the spectra of the $[M(NCO)_4]^{2-}$ ions. Thus the three highest energy bands of the complex anions can be assigned by direct analogy with the spectrum of silicon tetraisocyanate. Miller and Carlson found that their results for $Si(NCO)_4$ fitted a T_d model very well, except for one feature, the infrared-active deformation B mode (ν_{13}) (see Table 2 for the fundamental vibrations) which was tentatively assigned to a very weak band at 546 cm.$^{-1}$. In view of the assignment[4] of the infrared-active deformation B modes in pyramidal $P(NCO)_3$ at 388 and 316 cm.$^{-1}$, the above assignment of ν_{13} for the silicon compound seems unlikely. Further comparisons with linear four-atom deformation modes of this type are difficult to make. However, it is worth noting that the infrared-active ν_5 of C_2N_2 is observed[5] at 229 cm.$^{-1}$. The band at 338 cm.$^{-1}$ in the infrared spectrum of $Si(NCO)_4$ could thus be assigned as ν_{13} or ν_{14} with the other unobserved.

Miller and Carlson also assigned as ν_{13} a band at 528 cm.$^{-1}$ in the spectrum of germanium tetraisocyanate but, in this case, the band was very strong. Now the asymmetric stretching mode, ν_3, of silicon tetrachloride occurs at 608 cm.$^{-1}$ [6] and the SiN_4 degenerate stretch, ν_{11}, of silicon tetraisocyanate is found[3] at 727 cm.$^{-1}$. A similar order of difference might be expected in the case of the analogous compounds of germanium. Since ν_3 for $GeCl_4$ is[6] at 454 cm.$^{-1}$ an assignment of the strong band at 528 cm.$^{-1}$ in the spectrum of $Ge(NCO)_4$ as ν_{11}, rather than as ν_{13}, is not unreasonable. There is no difficulty in reassigning ν_{13} for $Ge(NCO)_4$ as the band at 259 cm.$^{-1}$ and ν_{14} as the previously unassigned band at 198 cm.$^{-1}$. These suggested reassignments in the infrared spectra of silicon and germanium tetraisocyanates do not require any changes in the Raman assignments, but neither do they solve the problem of the extra infrared band and the extra, polarized Raman line observed[3] for

TABLE 1.

Infrared data for $[Et_4N]_2[M(NCO)_4]$.

Condition	M = Mn	Fe	Co	Ni	Cu	Zn	Cd	$[Ph_4As]$ $[Fe(NCO)_4]$	Assignment *
$CH_3{\cdot}NO_2$	3502m	3509m	3517m	3509m	3506m	3524m	3497m	3546m	
$CH_3{\cdot}NO_2$	3395vw	3397vw	3401w	3395w	3413vvw	3410vw	3398vw	3406w	
$CH_3{\cdot}NO_2$					3390vvw				
Mull	3491w	3484w	3497w	3497m	3500m	3521w	3484w	3534w	
Mull	3382vw		3367vw	3378w	3378w	3408vw	3378vw		
$CH_3{\cdot}NO_2$	2196vvs	2199vvs	2206vvs	2208vvs	2222m	2208vvs	2195vvs	2199vvs	ν_9
$CH_3{\cdot}NO_2$					2198vvs				
Mull	2222sh		2217sh	2237sh	2247sh		2262sh	2208sh	
Mull	2174vs	2182vs	2179vs	2186vs	2183vs	2174vs	2174vs	2171vs	
$CH_3{\cdot}CN$	1321w	1322w	1325w	1321w	1318w	1326w	1319w	†	ν_{10}
Mull	1335m	1337w	1335w	1330w	1328w	1335w	1328w	1370vw	
Mull								837m	?
Acetone	625s	622s	619s	619s	620s	624s	622s	625s	ν_{12}
Acetone					615sh				
$PhNO_2$					617s				
$PhNO_2$					611sh				
Mull	623s	619m	620m	619sh	619m	623s	621s	626m	
			617sh	617s	617m			619m	
					612sh				
Mull	325s	325s	345s	341s	338s	321s	298s	410s	ν_{11}
Mull								239w	ν_{13}
Mull					213m				
$CH_3{\cdot}NO_2$						187w			ν_{13}

* Except for copper compound. † Region obscured.

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[3] Miller and Carlson, *Spectrochim. Acta*, 1961, **17**, 977.

[4] Miller and Baer, *Spectrochim. Acta*, 1962, **18**, 1311.

[5] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand and Co., Inc., Princeton, 1945.

[6] Nakamoto, " Infrared Spectra of Inorganic and Co-ordination Compounds," John Wiley and Sons, Inc., New York, 1963.

the germanium compound. The above new assignments lend support for the assignments made below for the bands at low energy observed for the $[M(NCO)_4]^{n-}$ ions.

$[M(NCO)_4]^{2-}$ *where* M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}, *and* Cd^{II}.—The infrared spectra of these ions in solution in the range 4000—400 cm.$^{-1}$ show only three bands which can be assigned as fundamentals. The bands of medium intensity at ~3500 cm.$^{-1}$ are combination bands. One band was observed in each case for the solid-state spectra in the range 400—200 cm.$^{-1}$. A solution of the zinc(II) complex was also examined in the range 200—150 cm.$^{-1}$ and showed a band at 187 cm.$^{-1}$. The simplicity of the spectra suggests very high symmetry for the complex anions, and the bands may be satisfactorily assigned on the basis of a T_d model.

The bands at ~2200 and ~1325 cm.$^{-1}$ can be assigned as ν_9 and ν_{10}, respectively, which are formally represented as stretching modes of the N–C–O group (see Table 2). Their positions show[3] that the cyanate groups are bonded through the nitrogen atoms. The sharp band at about 620 cm.$^{-1}$ in all the compounds is assigned as ν_{12}, the deformation *A* (see the foot of Table 2 for the representations of deformations *A* and *B*). There is no marked change in the position of this band when the mass of the metal is appreciably

TABLE 2.

Fundamental vibrations of $M(NCO)_4$ (T_d and D_{2d} models).

Description (for T_d model)	T_d	D_{2d} ‡
NCO pseudo-antisymm. stretch in phase (ν_1)	A_1 (R)	A_1 (R)
NCO pseudo-symmetric stretch in phase (ν_2)	A_1	A_1
M–N symmetric stretch (ν_3)	A_1	A_1
M–NCO deformation *A* * (ν_4)	*E* (R)	A_1 (R) B_1 (R)
M–NCO deformation *B* † (ν_5)	*E*	A_1 B_1
MN_4 deformation (ν_6)	*E*	A_1 B_1
M–NCO deformation *A* (ν_7)	T_1 (inactive)	A_2 (inactive) *E* (IR and R)
M–NCO deformation *B* (ν_8)	T_1	A_2 *E*
NCO pseudo-antisymm. stretch, out-of-phase (ν_9)	T_2 (IR and R)	B_2 (IR and R) *E* (IR and R)
NCO pseudo-symm. stretch, out-of-phase (ν_{10})	T_2	B_2 *E*
$M-N_4$ degenerate stretch (ν_{11})	T_2	B_2 *E*
M–NCO deformation *A* (ν_{12})	T_2	B_2 *E*
M–NCO deformation *B* (ν_{13})	T_2	B_2 *E*
$M-N_4$ deformation (ν_{14})	T_2	B_2 *E*

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

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

‡ IR = Infrared; R = Raman.

increased [*i.e.*, $Cd(NCO)_4^{2-}$]. However, this is not surprising in view of the nature of the deformation. In fact, the position of the band due to ν_{12} is only slightly removed in energy from the infrared-active deformation mode, ν_2, of the cyanate ion.[7]

The strong band found in the region 350—290 cm.$^{-1}$ for all these ions is assigned as ν_{11}, the metal–N_4 degenerate stretch, and the position of this band is dependent on the metal in much the same way as is ν_3, the metal–chlorine degenerate stretching frequency, of the MCl_4^{2-} ions.[8] However, it must be emphasized that this should not be thought of as a pure metal–nitrogen stretching frequency. The vibration can only be considered, rigorously, in terms of the molecule as a whole, since there will be coupling between this particular T_2 mode and the T_2 modes nearest in energy, namely ν_{12} and ν_{13}.

The band at 187 cm.$^{-1}$ in the spectrum of the tetraisocyanatozincate(II) ion is best assigned as ν_{13}. The deformation ν_4 of $ZnCl_4^{2-}$ is related to the mode ν_{14} of $M(NCO)_4^{n-}$ and is reported[8b] to be at 130 cm.$^{-1}$. Thus, ν_{14} for $[Zn(NCO)_4]^{2-}$ is not expected to be as high as 187 cm.$^{-1}$, and probably lies below the limit (150 cm.$^{-1}$) of this study.

The spectra of these ions thus fit a T_d model very well. Kinking of the M–N–C–O grouping will raise the degeneracy of the T_2 modes. However, the three highest-energy bands were examined under high resolution, but no splittings were observed, so any angular distortion of this type must be small.

The solid-state spectra of the isomorphous series of tetraethylammonium salts of the $[M(NCO)_4]^{2-}$ ions are very similar to the solution spectra. However, the N–C–O asymmetric stretching frequencies, ν_9, and the deformation *A* frequencies, ν_{12}, are broader, with the appearance of shoulders or small splittings in most cases. The spectra thus indicate some loss of symmetry in the solid state. This may be due either to the fact that the site symmetry of the complex anions in the solid state is less than T_d, or to a distortion of individual anions.

The infrared spectrum of solid n-butyltriphenylphosphonium tetraisocyanatocobaltate(II) [9] (2% pressed in polyethylene) has been obtained in the region 400—100 cm.$^{-1}$ by Professor A. J. Perkins of the Argonne National Laboratory.[10] Bands were observed at 345 and 185 cm.$^{-1}$. These agree well with the bands found for the tetraethylammonium salts.

Potassium Tetraisocyanatocobaltate(II).—The spectrum of this compound in the solid state is considerably more complicated than is that of the tetraethylammonium salt (Table 3). This compound has also been studied in the range 4000—80 cm.$^{-1}$ by Dr. G. L. Carlson of the Mellon Institute, who has kindly made his results available to us.[10] In the range 4000—400 cm.$^{-1}$ there is excellent agreement between the two sets of experimental results. We have not examined the spectrum below 400 cm.$^{-1}$ but Carlson's results in this region are also given in Table 3. The bands at 383, 359, and 205 cm.$^{-1}$ have also been observed independently by Professor Perkins for the compound pressed into polyethylene.[10]

TABLE 3.

Infrared data for $K_2Co(NCO)_4$.

Solid (*Nujol or halogenocarbon mulls*): 3521m, 3497m, ~3400w, br, 2695vvw, 2588vvw, 2299vvw, 2229vs, 2208vs, 2191vs, 2167vs, 2120sh, 2098m, 1389w, 1341w, ~1300sh, 653m, 641ms, 635ms, 626sh, 623s, 620sh, 383 * s, 359 * s, 205 * vs, ~160 * † s, br.

Solution: 2203vs (in acetone); 1325w (in CH_3CN); 619s (in acetone).

* Data of Dr. G. L. Carlson.[10] † Pressed in polyethylene.

We find that there is a considerable simplification of the spectrum for solutions of the compound in either acetone or acetonitrile. In particular, the complex band structures observed in the regions ~2200, ~1350, and ~620 cm.$^{-1}$ for the solid compound are replaced

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[7] Maki and Decius, *J. Chem. Phys.*, 1958, **28**, 1003.

[8] (*a*) Clark and Dunn, *J.*, 1963, 1198; (*b*) Sabatini and Sacconi, *J. Amer. Chem. Soc.*, 1964, **86**, 17.

[9] Cotton and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 1777.

[10] Personal communication.

in the solutions by single bands, the positions of which are in very good agreement with those observed for the solutions of the analogous tetraethylammonium salt. We conclude from these results that the tetraisocyanatocobaltate(II) ion suffers considerable loss of symmetry in the solid potassium salt. There is probably a strong interaction between the oxygen atoms of the cyanate groups and the potassium ions, leading to kinking of the M–N–C–O groups and possibly to a distortion of the Co–N$_4$ tetrahedron. The potassium cation would be more effective than the quaternary ammonium cation in this respect, being smaller and more polarizing. In this connection it is to be noted that the magnetic moment of the potassium salt is reported [9] to be somewhat lower than that of its n-butyltriphenylphosphonium analogue.

Tetraphenylarsonium Tetraisocyanatoferrate(III).—The spectrum of this compound in solution can also be satisfactorily interpreted on the basis of a T_d model. The higher oxidation state of the central atom appears to have little effect on the positions of the three highest-energy T_2 fundamentals. However, there is a marked increase in the energy of the ν_{11} mode, as compared with that of the iron(II) complex. This behaviour parallels that of the ν_3 mode for the corresponding chloro- and bromo-complexes.[8]

The solid-state spectrum of the iron(III) complex showed two bands, at 837 and 239 cm.$^{-1}$, which were not observed for the complexes of the bivalent metal ions. The band of medium intensity at 837 cm.$^{-1}$ did not occur in the solution spectrum, even with relatively concentrated solutions. Therefore we do not regard it as a fundamental. It is most probably a combination band, but without Raman data we cannot make a definite assignment. The weak band at 239 cm.$^{-1}$ we assign as ν_{13} but in the absence of solution data in this region this assignment must be regarded as tentative.

Tetraethylammonium Tetraisocyanatocuprate(II).—Whereas the solution spectra of the other first transition series bivalent metal complex ions show only three bands due to fundamentals in the region 4000—400 cm.$^{-1}$, the solution spectrum of the copper(II) complex has five bands in this region. In addition to these, two other bands were observed in the solid-state spectrum in the range 400—200 cm.$^{-1}$.

The effect on the vibrational modes of lowering the symmetry of the M(NCO)$_4$ species from T_d to D_{2d} is shown in Table 2. It is not necessary to invoke a symmetry lower than D_{2d} to explain the spectrum of the copper(II) complex. The two bands observed in the solution spectrum at ~2200 cm.$^{-1}$ can be assigned as the B_2 and E modes derived from the T_2 mode, ν_9, of T_d. Similarly, the two bands at ~620 cm.$^{-1}$ are the B_2 and E modes derived from ν_{12} of the T_d model. Cation absorption interfered with observation of the N–C–O pseudo-symmetric out-of-phase stretch, and only one band was found, although two are predicted. Only one band was observed in the region ~340 cm.$^{-1}$, but high resolution was not possible in this region. The band at 213 cm.$^{-1}$ is probably one of the three deformation B modes expected for D_{2d} symmetry. The infrared-active deformation A mode derived from the inactive ν_7 (T_1) of the T_d model was not observed, but is probably only very weakly allowed.

Structural Conclusions.—Our results show that in solution the overall symmetry of the ions [M(NCO)$_4$]$^{n-}$ is T_d, except when M = Cu^{II}. In these cases, therefore, the M–N–C–O groups appear to be linear, although small departures from linearity might not show up in the infrared spectra. The linearity of the grouping Si–N–C–O in silicon tetraisocyanate was interpreted [3] on the basis of a valence bond structure of the form $\overset{-}{\mathrm{Si}}\,\underline{\longleftarrow}\,\overset{+}{\mathrm{N}}{=}\mathrm{C}{=}\mathrm{O}$. With the transition metal complex anions we have studied p_π–d_π bonding seems less likely and we suggest that of the possible canonical forms, that of the type $\mathrm{M}{-}\overset{+}{\mathrm{N}}{\equiv}\mathrm{C}{-}\overset{-}{\mathrm{O}}$ predominates.

The lowering of symmetry from T_d to D_{2d} in the copper(II) complex could be caused either by kinking of the Cu–N–C–O groups or by deformation of the CuN$_4$ tetrahedron. We prefer the latter alternative for the following reasons. First, the other tetraethylammonium salts contain linear M–N–C–O groups, and there seems to be no reason why the copper compound should be anomalous in this respect. Secondly, the electronic spectra[1] are in accord with a distorted CuN_4 tetrahedron. Moreover, the ions $CuCl_4^{2-}$ and $CuBr_4^{2-}$ are known to have distorted tetrahedral structures in the solid state.[11] Thus both the vibrational and the electronic spectrum of the tetraisocyanatocuprate(II) ion can be rationalized on the basis of a distorted CuN_4 tetrahedron. Now the ground electronic state of the copper ion, after application of spin-orbit coupling, is a Kramers doublet, Γ_7, and is therefore not susceptible to Jahn-Teller splitting.[12] Since we cannot invoke crystal forces to explain the distortion, and the other ions were studied in the same solvents, we conclude that the distortion observed for the copper(II) complex is an inherent one, though the reasons for this are not yet clear.

EXPERIMENTAL

The preparation of the compounds $[Et_4N]_2[M(NCO)_4]$ where M = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, has been described.[1] However, use of nitromethane as the exchange medium instead of acetone gives a much improved yield and a purer initial product. The preparation of $[Et_4N]_2[Fe(NCO)_4]$ will be described.[13]

Tetraethylammonium Tetraisocyanatocadmate(II).—Tetraethylammonium tetrabromocadmate(II) (4·0 g.) was shaken for 30 min. with an excess of silver cyanate (~4 g.) in nitromethane (30 ml.). The mixture was filtered and diethyl ether was added to the filtrate. Colourless *crystals* formed, which were purified by re-dissolving in nitromethane, filtering the solution and reprecipitating the *complex* by addition of diethyl ether (61% yield, m. p. 170°) (Found: C, 43·9; H, 7·5; N, 15·5. $C_{20}H_{40}CdN_6O_4$ requires C, 44·4; H, 7·4; N, 15·5%). The complex is hydroscopic and is decomposed immediately by water and alcohols. It is isomorphous with its cobalt(II) analogue.

Tetraphenylarsonium Tetraisocyanatoferrate(III).—Tetraphenylarsonium tetrachloroferrate(III) (3·0 g.) was shaken with silver cyanate (3·2 g.) in acetone (25 ml.) for 1 hr. The mixture was filtered into excess of diethyl ether. Orange *crystals* separated and were purified by dissolving in acetone, filtering the solution, and evaporation to dryness (70% yield, m. p. 159°) (Found: C, 56·1; H, 3·45; O, 10·9. $C_{24}H_{20}AsFeN_4O_4$ requires C, 55·4; H, 3·3; O, 10·5%).

Potassium tetraisocyanatocobaltate(II) was supplied by Dr. M. Goodgame.

Infrared spectra were recorded with a Grubb-Parsons Spectromaster grating spectrometer in the region 4000—400 cm.$^{-1}$, and with a Grubb-Parsons double-beam grating spectrometer, type D.M.2, in the region 450—200 cm.$^{-1}$. The infrared spectrum of tetraethylammonium tetraisocyanatozincate(II) in nitromethane was recorded in the region 200—150 cm.$^{-1}$ using an evacuated single-beam grating instrument, designed and built by Dr. J. L. Wood and Dr. P. Taimsalu.[14] The Raman spectrum of $[Et_4N]_2[Zn(NCO)_4]$ in nitromethane solution was recorded with a Cary model 81 spectrometer.

Solution spectra were recorded in the region 4000—400 cm.$^{-1}$ using solution cells fitted with potassium bromide windows, and in the region 200—150 cm.$^{-1}$ polyethylene windows were used. The solid-state spectra were obtained using the Nujol mull technique. The mulls were supported between potassium bromide plates for the range 4000—400 cm.$^{-1}$ and polyethylene plates below 400 cm.$^{-1}$.

The compounds $[Et_4N]_2[MnBr_4]$ and $[Ph_4As][FeCl_4]$ were used as control compounds to identify the bands in the spectra due to cation absorption. Cation absorption interfered in one region only, the isocyanate symmetric stretching region, 1400—1300 cm.$^{-1}$.

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