tivities are shown in Table II. Figure 4 shows the resolved spectra of all the various species.

TABLE II

ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES OF THE PALLADIUM–CHLORIDE–BROMIDE MIXED SPECIES

Species	Absorption maxima, mμ	Molar absorptivity, $\epsilon_{max} \times 10^{-3}$
$PdCl_4^{2-}$	279 ± 1	11.2 ± 0.05
	222 ± 1	33.1 ± 0.1
$PdCl_3Br^{2-}$	295 ± 5	11.3 ± 0.2
$PdCl_2Br_2^{2-}$	305 ± 5	10.3 ± 0.2
$PdClBr_3^{2-}$	310 ± 5	11.4 ± 0.2
$PdBr_4^{2-}$	332 ± 1	11.5 ± 0.05
	246 ± 1	32.1 ± 0.1

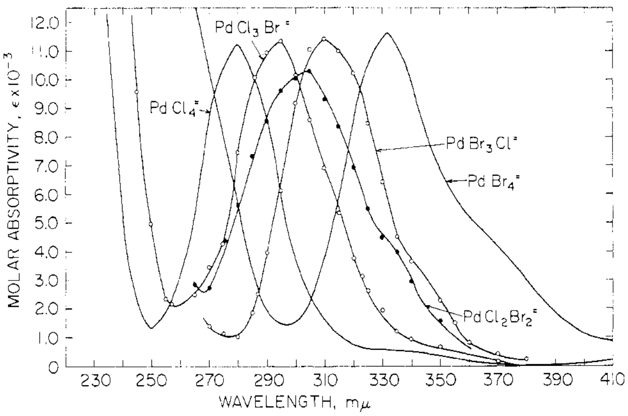

Figure 4.—Resolved spectra of palladium–chloride–bromide mixed complexes.

The constants for the formation of the three mixed species from the parent reactants along with the statistically predicted values are shown in Table III.

TABLE III

STATISTICAL AND OBSERVED VALUES OF THE FORMATION CONSTANTS

Reaction	Log K (found)	Log K (statistical)
$^3/_4PdCl_4^{2-} + ^1/_4PdBr_4^{2-} \rightleftharpoons PdCl_3Br^{2-}$	0.52 ± 0.05	0.60
$^1/_2PdCl_4^{2-} + ^1/_2PdBr_4^{2-} \rightleftharpoons PdCl_2Br_2^{2-}$	0.57 ± 0.06	0.78
$^1/_4PdCl_4^{2-} + ^3/_4PdBr_4^{2-} \rightleftharpoons PdClBr_3^{2-}$	0.49 ± 0.05	0.60

In many other systems the stabilities of the mixed ligand complexes are greater than would be predicted on a statistical basis.[5] However, in this system, it appears that the statistical constants are slightly higher than or, within experimental error, equal to the measured values.

Future studies will be made on the palladium system with Cl^- and I^- and with Br^- and I^-. It will be interesting to see if the stability constants in these systems are greater or smaller than the statistically predicted values.

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(5) (a) Y. Marcus and I. Eliezer, *J. Phys. Chem.*, **66**, 1661 (1962); (b) Y. Marcus, I. Eliezer, and M. Zangen, "Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, Sept 1964," Akademiai Kiado, Publishing House of the Hungarian Academy of Sciences, Budapest, 1965, pp 409–418.

CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY

Synthesis and Vibrational Spectra of $[Co(N_3)_4]^{2-}$, $[Zn(N_3)_4]^{2-}$, and $[Sn(N_3)_6]^{2-}$ [1]

BY DENIS FORSTER AND WILLIAM DEW. HORROCKS, JR.

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The tetraethylammonium salts of the complex anions $[Co(N_3)_4]^{2-}$, $[Zn(N_3)_4]^{2-}$, and $[Sn(N_3)_6]^{2-}$ were synthesized and the infrared spectra of the solids and of solutions were recorded in the 200–4000-cm^{-1} region. The Raman spectra of the zinc and tin compounds were measured. A vibrational analysis of a hypothetical T_d $Zn(N_3)_4^{2-}$ ion was carried out as an aid in making the assignments. The spectra indicate a nonlinear M–N–N linkage. Vibrational assignments were made on the basis of D_{2d} symmetry for the tetracoordinated species and D_{3d} symmetry for the hexacoordinated tin complex.

Introduction

Very little information is available on the vibrational spectra of azido complexes. This is principally because many of the simple metal azides, *e.g.*, AgN_3 and $Hg(N_3)_2$, are highly explosive compounds. The herein reported preparation of stable complex anions containing azide groups allows a more thorough investigation of the vibrational spectra of coordinated azide ions.[2a] Of particular interest is the determination of whether the coordination is such that the M–N–N configuration is linear or bent. As typical of tetrahedral complexes of divalent metals, the salts $[(C_2H_5)_4N]_2[M(N_3)_4]$ where M = Co, Zn were synthesized. $[(C_2H_5)_4N]_2[Sn(N_3)_6]$ provides an example of octahedral hexacoordination by the azide ion. The colorless zinc and tin complexes were chosen because of their suitability for Raman investigation.

Experimental Section

Preparation of the Complexes. $[(C_2H_5)_4N]_2[Co(N_3)_4]$.—$[(C_2H_5)_4N]_2[CoCl_4]$ (1.0 g) was shaken with an excess of finely powdered sodium azide (~1 g) in acetone (~20 ml) for about 4 hr. The resulting blue solution was filtered, and diethyl ether was added to the filtrate. The precipitated solid was purified

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(1) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF-49(638)-1492.

(2) (a) The apparent stability of the compounds described here has not prevented the authors from exercising great care in their handling. Similar caution is advocated in any further work with these compounds. (b) P. Sensise, *J. Am. Chem. Soc.*, **81**, 4196 (1959).

TABLE I

VIBRATIONAL SPECTRA OF TETRAHEDRAL AZIDO COMPLEXES (cm^{-1})

$[(C_2H_5)_4N]_2[Co(N_3)_4]$		$[(C_2H_5)_4N]_2[Zn(N_3)_4]$				
Infrared		Infrared		Raman		
Solid	Soln	Solid	Soln	Solid	Soln[d]	Assignment
~3420 vw						$2091 + 1338 = 3429$
~3360 mw						
			~3435 sh[a]			$2097 + 1341 = 3438$ and $2102 + 1341 = 3443$
		~3370 w, br	~3370 mw, br[a]			$1288 + 2102 = 3390$
			~3330 sh[a]			$1288 + 2062 = 3350$
					~2102 vvw(p)[a]	A_1 N_3 pseudo-antisym str in phase
2089 m	2091 m[b,e]	2098 m	2097 m[a]			B_2 N_3 pseudo-antisym str out of phase
~2050 vs, br	2054 vs[b,e]	~2055 vs, br	2062 vs[a]		2063 vvw[a]	E N_3 pseudo-antisym str out of phase
				1348 m	1346 m(p)[a]	A_1 N_3 pseudo-sym str in phase
~1338 mw	1338 m[c]	1342 m	1341 mw[c]			E N_3 pseudo-sym str out of phase
~1280 vw	1280 vw[c]	~1290 vw	1288 vw[c]			B_2 N_3 pseudo-sym str out of phase
~642 m, br	640 m[b]	649 m, br	649 m[b]			E MN_3 def A
610 m	611 m[b]	615 m	615 m[b]			B_2 MN_3 def A
				362 m	360 m(p)[a]	A_1 M–N sym str
368 s, br	371 s[a]	351 s, br	350 s, br[a]			E M–N str
		~295 vw				B_2 M- N str?

[a] In nitromethane. [b] In acetone. [c] In acetonitrile. [d] ~2 M in nitromethane; p = polarized. [e] The corresponding bands in $[(C_6H_5)_4As]_2[Co(N_3)_4]$ were found at 2090 and 2054 cm^{-1} in acetone.

by dissolving in nitromethane and reprecipitating with ether; 80% yield; mp 181° dec.

Anal. Calcd for $C_{16}H_{40}CoN_{14}$: C, 39.45; H, 8.21; N, 40.24. Found: C, 39.59; H, 8.40; N, 40.35.

$[(C_6H_5)_4As]_2[Co(N_3)_4]$.—This compound was prepared by the method described above; 77% yield; mp 154° (lit.[2b] 153–154°). It was previously prepared by a much less convenient method involving aqueous solutions.

$[(C_2H_5)_4N]_2[Zn(N_3)_4]$.—This complex was prepared by the method described above for the analogous cobalt compound; 80% yield; mp 193° (effervescence begins ~200°).

Anal. Calcd for $C_{16}H_{40}N_{14}Zn$: C, 38.94; H, 8.10; N, 39.71. Found: C, 38.79; H, 8.07; N, 39.41.

$[(C_2H_5)_4N]_2[Sn(N_3)_6]$.—This compound was prepared from $[(C_2H_5)_4N]_2[SnCl_6]$ by the exchange method described above for the preparation of $[(C_2H_5)_4N]_2[Co(N_3)_4]$. In this case the mixture was shaken for 18 hr; yield 75%; mp 280–284° dec.

Anal. Calcd for $C_{16}H_{40}N_{20}Sn$: C, 30.46; H, 6.34; N, 44.38. Found: C, 30.20; H, 6.24; N, 44.13.

The compound does not detonate on rapid heating or from shock. It is slightly hygroscopic and acetone solutions of the complex become turbid on standing presumably owing to hydrolysis caused by atmospheric moisture.

Attempts to Prepare $Ni(N_3)_4^{2-}$ and $Pd(N_3)_4^{2-}$.—All efforts to obtain a compound containing the $Ni(N_3)_4^{2-}$ ion by exchange of compounds of the type $[cation]_2[NiCl_4]$ with sodium azide led to yellow, explosive compounds presumably containing bridging azide groups even when the cation used was very large, such as $(C_6H_5)_4As^+$. This situation resembles that found for $Ni(NCS)_4^{2-}$ [3] except that the $Ni(N_3)_4^{2-}$ ion does not appear to exist even in solution.

Attempts to prepare compounds containing the $Pd(N_3)_4^{2-}$ ion gave brown solids which exploded on heating and had analyses inconsistent with a formulation based on a $Pd(N_3)_4^{2-}$ ion.

Spectra.—Infrared spectra were obtained using a Beckman IR 12 grating spectrophotometer. Solutions were examined in cells fitted with cesium iodide windows and solids as Nujol mulls. Raman spectra were recorded with a Cary 81 Raman spectrometer.

Results and Discussion

The method described here for the preparation of azido complexes is related to the method used to prepare alkyl azides by refluxing an alkyl halide with sodium azide in a water–ethanol mixture.[4] The solvent system used in the organic preparation is not suitable for most metal coordination compounds because of hydrolysis under these conditions. Acetone proved to be much more suitable because of the slight solubility of sodium azide and the insolubility of the unwanted reaction product, sodium chloride, in this medium.

The infrared spectra between 4000 and 200 cm^{-1} of $[(C_2H_5)_4N]_2[Co(N_3)_4]$, $[(C_2H_5)_4N]_2[Zn(N_3)_4]$, and $[(C_2H_5)_4N]_2[Sn(N_3)_6]$ in solution and as solids were recorded. The Raman spectra of $[(C_2H_5)_4N]_2[Zn(N_3)_4]$ in nitromethane and as a solid and of $[(C_2H_5)_4N]_2[Sn(N_3)_6]$ in nitromethane were obtained. Although many metal complexes are solvolyzed in polar oxy solvents, the great similarity between the solid and solution data leaves no doubt that the species studied in solution are indeed the entities formulated.

$Co(N_3)_4^{2-}$ and $Zn(N_3)_4^{2-}$ Ions.—The infrared data for $[(C_2H_5)_4N]_2[Co(N_3)_4]$, $[(C_2H_5)_4N]_2[Zn(N_3)_4]$, and also $[(C_6H_5)_4As]_2[Co(N_3)_4]$ are presented in Table I, along with Raman data for $[(C_2H_5)_4N]_2[Zn(N_3)_4]$.

A description of the fundamental vibrations of an $M(ABC)_4$ species with T_d or D_{2d} symmetry has been given.[5] In order to determine the regions where the fundamentals of the azido complexes would be expected, we have carried out a vibrational analysis of the $Zn(N_3)_4^{2-}$ ion assuming T_d symmetry.

The symmetry coordinates and *F*-matrix elements of an $M(XYZ)_4$ entity will be reported later in conjunction with a normal coordinate analysis of the $Zn(NCS)_4^{2-}$ ion.[6] The *G*-matrix elements were calculated using a computer program developed by Schachtschneider.[7] The bond distances used in cal-

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(3) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 823 (1965).

(4) W. Theilheimer, Ed., "Synthetic Methods of Organic Chemistry," Vol. 11, S. Karger, New York, N. Y., 1957, p 528.

(5) F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, **17**, 977 (1961).

(6) D. Forster and W. DeW. Horrocks, Jr., to be published.

(7) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **19**, 117 (1963).

culating the *G*-matrix elements were estimated from the X-ray crystal structure determination of $Co(NH_3)_5N_3^{2+}$.[8] A slightly longer metal–nitrogen distance was used for the zinc complex than that found for the cobalt compound, in accord with the usual trend on going from a trivalent to a divalent ion. Thus, the bond distances used for the $Zn–N_1–N_2–N_3$ grouping were: $Zn–N_1 = 2.00$ A, $N_1–N_2 = 1.21$ A, and $N_2–N_3 = 1.14$ A. The secular equation was then solved with a computer program also developed by Schachtschneider[7] using a set of approximate force constants chosen as follows. The $N_1–N_2$ and $N_2–N_3$ stretching force constants were taken to be perturbations of the free-ion N–N stretching force constant of 13.7 mdynes/A.[9] The N–N–N bending force constant was set equal to the free-ion value.[9] The Zn–N–N and N–Zn–N bending force constants were taken to have the same value as the corresponding constants in $Zn(CN)_4^{2-}$.[10] The Zn–N force constant for the T_2 block was taken to be slightly greater than the Zn–C force constant in $Zn(CN)_4^{2-}$ and the Zn–N, Zn–N stretch–stretch interaction has been taken to be about the same as the corresponding interaction in the cyanide complex. Two off-diagonal force constants were included; the N_1-N_2, N_2-N_3 stretch–stretch interaction was set equal to the free-ion value,[9] and a small N–N–N, Zn–N–N bend–bend interaction was introduced. The latter was included because of the very large bend–bend interaction constants that have been found in carbon suboxide and related molecules[11] where two linear bends can also interact directly. In Table II a list of the force constants is given together with the calculated frequencies. In the related $Zn(CN)_4^{2-}$ and $Ni(CO)_4$ entities, interaction constants between the bends lead to T_1 frequencies lower than the corresponding T_2 frequencies. We have not included these interactions and thus our calculated T_1 frequencies are almost certainly too high. No attempt has been made to refine the force constants because we do not consider the $Zn(N_3)_4^{2-}$ ion to have T_d symmetry. The effect of having nonlinear Zn–N–N–N groups will be to lift the degeneracy of the T_d fundamentals. However, it must be borne in mind that the differences between the resulting fundamentals will depend upon differences in interaction constants which in turn depend upon coupling *via* the central metal and interactions between nonbonded groups. Now the Zn–N force constant is small and the closest nonbonded N–N distance is 3.27 A; we therefore anticipate that a $Zn(N_3)_4^{2-}$ ion with a symmetry lower than T_d will have a spectrum very similar to that of a T_d species with the T_2 fundamentals of T_d split by a small amount.

The experimentally observed frequencies in Table I strongly suggest that the symmetry of the $Zn(N_3)_4^{2-}$ ion is lower than T_d. This is emphasized when a comparison is made between the isoelectronic pair of ions, $Zn(NCO)_4^{2-}$ and $Zn(N_3)_4^{2-}$. (See Table III.)

TABLE II

CALCULATED FREQUENCIES OF A HYPOTHETICAL T_d $Zn(N_3)_4^{2-}$ ION USING FORCE CONSTANTS TAKEN FROM RELATED MOLECULES

	F-matrix elements	Calcd frequencies, cm^{-1}
A_1	$F_{N_2N_3} = 15.6$[a]	N_3 pseudo-antisym str in phase = 2059
	$F_{N_1N_2} = 10.3$	N_3 pseudo-sym str in phase = 1363
	$F_{ZnN} + 3F'_{ZnN,ZnN} = 2.7$	Zn–N sym str = 310
	$F'_{N_1N_2,N_2N_3} = 1.7$	
E	$F_{NNN} = 0.75$[b]	MN_3 def A = 644
	$F_{ZnNN} = 0.25$	MN_3 def B = 209
	$F_{NZnN} = 0.23$	NZnN def = 41
	$F'_{NNN,ZnNN} = 0.05$	
T_1	$F_{NNN} = 0.75$	MN_3 def A = 641
	$F_{ZnNN} = 0.25$	MN_3 def B = 179
	$F'_{NNN,ZnNN} = 0.05$	
T_2	$F_{N_2N_3} = 15.6$	N_3 pseudo-antisym str out of phase = 2057
	$F_{N_1N_2} = 10.3$	N_3 pseudo-sym str out of phase = 1332
	$F_{NNN} = 0.75$	MN_3 def A = 644
	$F_{ZnN} - F'_{ZnN,ZnN} = 1.6$	Zn–N str = 345
	$F_{ZnNN} = 0.25$	MN_3 def B = 203
	$F_{NZnN} = 0.23$	N–Zn–N def = 46
	$F'_{N_2N_3,N_1N_2} = 1.7$	
	$F'_{NNN,ZnNN} = 0.05$	

[a] Stretching force constants are given in mdynes/A. [b] Bending force constants are given in mdyne-A/radian^2.

TABLE III

COMPARISON BETWEEN THE INFRARED SPECTRA OF $Zn(NCO)_4^{2-}$ AND $Zn(N_3)_4^{2-}$ (CM^{-1})[a]

$Zn(NCO)_4^{2-}$	$Zn(N_3)_4^{2-}$
2208 vs	2097 m
	2062 vs
1326 w	1342 mw
	1288 vw
624 s	649 m
	615 m
321 s	350 s
	~295 vw (solid)?
187 w	

[a] These are solution measurements in the same solvents.

Now in a previous study[12] of $Zn(NCO)_4^{2-}$, the infrared fundamentals were observed as single bands, which was taken to indicate that any departure from T_d symmetry is small. The additional bands observed in the azido complex we take to be fundamentals and the spectrum is assigned on the basis of D_{2d} symmetry (see Table I). The only band in the azide complex which it appears possible to explain on the basis of T_d symmetry is the one at 1288 cm^{-1}. This could be a combination or overtone of the N–N–N bending fundamentals.

Similar conclusions may be drawn about the $Co(N_3)_4^{2-}$ ion from a comparison with the spectrum of the isoelectronic $Co(NCO)_4^{2-}$.[12]

There is no reason to anticipate a distortion of the primary "coordination sphere" in a tetrahedral zinc or cobalt complex with four identical ligands. The lowering of symmetry from T_d in the azido complexes

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(8) G. J. Palenik, *Acta Cryst.*, **17**, 360 (1964).
(9) P. Gray and T. C. Waddington, *Trans. Faraday Soc.*, **53**, 901 (1957).
(10) L. H. Jones, *Spectrochim. Acta*, **17**, 188 (1961).
(11) W. H. Smith, private communication.
(12) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 262 (1965).

must thus be attributed to a nonlinearity of the M–N–N–N groups. The crystal structure determination of $Co(NH_3)_5N_3^{2+}$ shows[8] that the N–N–N grouping retains its linearity but that the Co–N–N angle is 125°. The most likely explanation of the spectra of the tetraazido complexes is that a similar distortion exists.

No attempt has been made to extend our vibrational analysis to a D_{2d} structure because the Zn–N–N angle is not known.

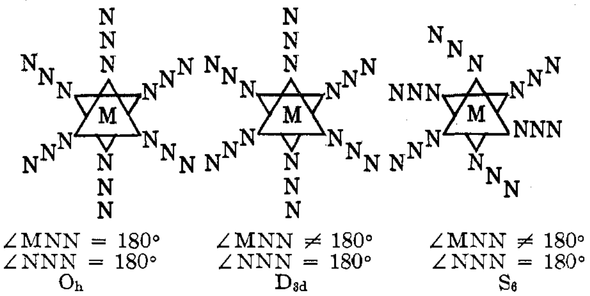
The $Sn(N_3)_6^{2-}$ Ion.—The results of the infrared and Raman study of $[(C_2H_5)_4N]_2[Sn(N_3)_6]$ are presented in Table IV. The fundamental modes of an M-(NNN)$_6$ entity with O_h, D_{3d}, or S_6 symmetry (shown schematically below) are given in Table V.

TABLE IV

VIBRATIONAL SPECTRUM OF $[(C_2H_5)_4N]_2[Sn(N_3)_6]$ (CM^{-1})

Infrared		Raman	
Solid	Soln	Soln[d]	Assignment[e]
	~3430 vw, br[a]		
~3380 vw, br	~3395 w, sh[a]		
~3340 w, br	~3350 mw, br[a]		
2615 vw			
		2113 s(p)	ν_1
2115 m	2112 m[a]		ν_{17}
2080 vs	2080 vs[a]		ν_{18}
		2078 m	ν_4
		1348 ms(p)	ν_2
1340 m	1342 m[b]		ν_{19}
1288 s	1289 s[b]		ν_{20}
1100 vvw			
1056 vvw			
659 s, br	662 s[c]		ν_{24}
601 m, s	602 m, s[c]		ν_{23}
		399 vs(p)	ν_3
~390 s, br	391 s[a]		ν_{22}
~330 w, sh	~335 w, sh[a]		ν_{21}
		335 m	ν_6
~220 s, br	232 s[a]		ν_{26}
		202 m	ν_{14}

[a] In nitromethane. [b] In acetonitrile. [c] In acetone. [d] ~1 *M* in nitromethane. [e] See Table V.



In Table VI we compare the infrared spectra of the *isoelectronic* pair of ions $Sn(NCO)_6^{2-}$ and $Sn(N_3)_6^{2-}$.

The ions were studied in the same solvents, except for two regions of the $Sn(NCO)_6^{2-}$ spectrum which are solid-state measurements. There is obviously a great similarity between the two spectra. However, there are extra bands in the fundamental regions of the azido complex. The spectrum of the $Sn(NCO)_6^{2-}$ ion was interpreted[13] on the basis of O_h symmetry.

TABLE V

FUNDAMENTAL VIBRATIONS FOR M(NNN)$_6$ AND CORRELATION TABLE FOR O_h, D_{3d}, AND S_6 SYMMETRIES

Description	O_h sym (activity)	No.	D_{3d} sym (activity)	S_6 sym (activity)
N_3 pseudo-antisym str in phase	A_{1g} (Raman)	1	A_{1g} (Raman)	A_g (Raman)
N_3 pseudo-sym str in phase	A_{1g}	2	A_{1g}	A_g
M–N sym str	A_{1g}	3	A_{1g}	A_g
N_3 pseudo-antisym str	E_g (Raman)	4	E_g (Raman)	E_g (Raman)
N_3 pseudo-sym str	E_g	5	E_g	E_g
M–N str	E_g	6	E_g	E_g
M–N–N–N def A[a]	T_{1g} (inactive)	7	A_{2g} (inactive)	A_g
		8	E_g (Raman)	E_g
M–N–N–N def B[b]	T_{1g}	9	A_{2g}	A_g
		10	E_g	E_g
M–N–N–N def A	T_{2g} (Raman)	11	A_{1g}	A_g
		12	E_g	E_g
M–N–N–N def B	T_{2g}	13	A_{1g}	A_g
		14	E_g	E_g
N–M–N def	T_{2g}	15	A_{1g}	A_g
		16	E_g	E_g
N_3 pseudo-antisym str out of phase	T_{1u} (infrared)	17	A_{2u} (infrared)	A_u (infrared)
		18	E_u (infrared)	E_u (infrared)
N_3 pseudo-sym str out of phase	T_{1u}	19	A_{2u}	A_u
		20	E_u	E_u
M–N str	T_{1u}	21	A_{2u}	A_u
		22	E_u	E_u
M–N–N–N def A	T_{1u}	23	A_{2u}	A_u
		24	E_u	E_u
M–N–N–N def B	T_{1u}	25	A_{2u}	A_u
		26	E_u	E_u
M–M–N def	T_{1u}	27	A_{2u}	A_u
		28	E_u	E_u
M–N–N–N def A	T_{2u} (inactive)	29	A_{1u} (inactive)	A_u
		30	E_u	E_u
M–N–N–N def B	T_{2u}	31	A_{1u}	A_u
		32	E_u	E_u
N–M–N def	T_{2u}	33	A_{1u}	A_u
		34	E_u	E_u

[a] deformation A may be represented by $\overset{\uparrow}{M}-\underset{\downarrow}{N}-\overset{\uparrow}{N}-\underset{\downarrow}{N}$. [b] Deformation B may be represented by $\overset{\uparrow}{M}-\underset{\downarrow}{N}-\overset{\uparrow}{N}-N$.

TABLE VI

COMPARISON OF THE INFRARED SPECTRA OF $Sn(NCO)_6^{2-}$[a] AND $Sn(N_3)_6^{2-}$ (CM^{-1})

$Sn(NCO)_6^{2-}$	$Sn(N_3)_6^{2-}$
2183 vs	2112 m
	2080 vs
1307 vw (solid)	1342 m
	1289 s
622 s	662 s
	602 ms
383 vs	391 s
	~335 w, sh
235 s (solid)	232 s
216 s (solid)	

[a] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1286 (1965).

It is not possible to give a plausible explanation for the spectrum of the $Sn(N_3)_6^{2-}$ ion without invoking a symmetry lower than O_h. As with the tetrahedral anions, nonlinear M–N–N–N groups must be present to explain this. If the threefold axis and center of symmetry are retained, then a D_{3d} structure is obtained as shown. This is the structure adopted by the $Rh(SCN)_6^{3-}$ ion in the solid state.[14] A further possibility is that the twofold axis is lost but the center of symmetry is retained giving an S_6 structure. This model has less steric interaction between the azide groups. However, there are certain difficulties in

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(13) See footnote *a* of Table VI.

(14) Z. V. Zvonkova, *Zh. Fiz. Khim.*, **26**, 1798 (1952).

assigning the vibrational spectrum of the $Sn(N_3)_6^{2-}$ ion on the basis of D_{3d} or S_6 symmetry. Since both structures have a center of symmetry, the rule of mutual exclusion should apply. However, it can be seen that three of the infrared fundamentals—2112, 2080, and 335 cm^{-1}—appear to have Raman counterparts at 2113, 2078, and 335 cm^{-1}. The 2112–2113-cm^{-1} coincidence can be dismissed as accidental since, even if the anion loses its center of symmetry and has the point group D_3, the A_1 modes do not become infrared active and the 2113-cm^{-1} Raman band is polarized. An accidental coincidence of the 2080 and 2078 cm^{-1} modes is also possible since differences in these modes depend upon coupling of the azide vibrations *via* several bonds and the heavy central metal atom which may be weak. The occurrence of a band at 335 cm^{-1} in both the Raman and infrared spectra cannot be so readily dismissed as accidental. This coincidence could indicate a D_3 point group for the anion in which case 21 infrared-active fundamentals are allowed above 200 cm^{-1} whereas only eight or nine are observed. Many of the 21 infrared-active fundamentals of D_3 would be expected to have very low intensity, and thus it is not possible to rule out this structure entirely. If there were relatively free rotation about the Sn–N bonds, there is a possibility of population of some low-symmetry forms. However, the Raman polarization data militate against this. The best explanation of the observed spectrum is to assume that the 335-cm^{-1} coincidence is accidental and therefore the frequencies have been tentatively assigned on the basis of D_{3d} symmetry, although a decision between D_{3d} and S_6 symmetry on the basis of the vibrational spectrum is virtually impossible.

Contribution from The William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1, England

Peroxo Complexes of Cobalt(III) with a Cyclic Quadridentate Secondary Amine

By B. BOSNICH, C. K. POON, and M. L. TOBE

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A number of complex cobalt(III) cations, having the stoichiometry $[Co(cyclam)XO]^{n+}$ (where cyclam = 1,4,8,11-tetraazacyclotetradecane and X = Cl, N_3, H_2O, NCS, or NO_2), have been isolated and their chemical and physical properties examined. These complexes are the first stable species that can be isolated during the aerial oxidation of aqueous solutions containing cobaltous salts and the tetramine. The properties indicate that the complexes are dimeric, with a peroxo bridge between two tervalent cobalt atoms and a *trans* disposition of the cyclic ligand. In the presence of acid (HY), the peroxo bridge is broken and mixed complex cations of the type *trans*-$[Co(cyclam)XY]^{n+}$ can be obtained.

Introduction

The ability of ammoniacal solutions of cobaltous salts to absorb atmospheric oxygen has been known for many years.[1] Except for a few cases,[2] this process is irreversible and leads to the formation of the relatively unstable peroxo complexes[1] that probably exist in the deep brown solutions formed in the preparation of cobalt(III) complexes by aerial oxidation.

In the course of the study of the properties and the chemical kinetics of complexes containing the cyclic quadridentate ligand 1,4,8,11-tetraazacyclotetradecane (cyclam), it was found that the brown species formed during the preparation of the cobalt(III) complexes[3] were relatively stable, and, furthermore, provided us with suitable intermediates for the preparation of complex cations of the type *trans*-$[Co(cyclam)XY]^{n+}$, which were required for the kinetic investigations and which were difficult to prepare in adequate amounts by other methods. This paper describes the preparation of these peroxo complexes and their physical and chemical properties.

Results and Discussion

Two methods have been used in order to synthesize these complexes. In the first, which is suitable for X = Cl, NO_2, and NCS, a solution of cobaltous perchlorate was slowly added to an aqueous solution of cyclam and a suitable salt of the appropriate anion. The color immediately changed to dark brown, indicating an extremely rapid uptake of dissolved oxygen, and the appropriate complexes slowly crystallized out on standing. In the absence of coordinating anions the aquo complex, *trans*-$[H_2OCo(cyclam)O_2(cyclam)CoH_2O](ClO_4)_4$, was obtained and the coordinated water could be replaced readily by other ligands. This formed the basis of the second method of preparation, which could be used to obtain all the complexes listed above as well as the azido complex, which could not be obtained by the first method.

These compounds are insoluble in most common organic solvents and are sparingly soluble in water where they slowly decompose to produce the *trans*-$[Co(cyclam)XH_2O]^{2+}$ cations; they are, however, quite stable

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(1) J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 361 (1964), and references therein.

(2) L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963), and references therein.

(3) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).