CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF WATERLOO, WATERLOO, ONTARIO, CANADA, AND
THE UNIVERSITY OF CALGARY, CALGARY, ALBERTA, CANADA

Solid-State Structures of Group IIIb Metal Chloride Adducts with 2,2',2''-Terpyridyl

BY G. BERAN, K. DYMOCK, H. A. PATEL,
A. J. CARTY,* AND P. M. BOORMAN

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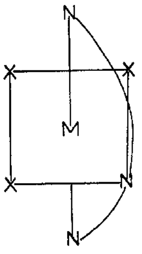
Considerable progress has been made in recent years toward an understanding of the solid-state structures of group IIIb metal halide adducts with neutral nitrogen donors.[1] Structural information has, for the most part, been obtained from far-infrared and Raman studies on crystalline solids.[2-8] Single-crystal X-Ray structural determinations have established the detailed molecular stereochemistry in $[GaCl_2(bipy)_2][GaCl_4]$ (bipy = 2,2'-bipyridyl)[9] and $GaCl_3$(terpy) (terpy = 2,2',2''-terpyridyl).[10] Vibrational spectroscopy has been most useful in the identification of tetrahalometalate ions MX_4^- (M = Ga, In, Tl; X = Cl, Br, I) in the crystal lattices of complexes having ionic dimer structures.[4-6] In other cases however an unambiguous structural assignment may not be possible from solid-state infrared and Raman data. The complexes MCl_3(terpy) (M = Ga, In, Tl) appeared to be representative of the latter situation since limited spectroscopic studies on $TlCl_3$(terpy)[4] and $GaCl_3$(terpy)[10] did not suffice to distinguish the trans octahedral structure I from the alternative ionic formulation II in which the cation (M = Ga, In) is isoelectronic (and presumably isostructural) with the trigonal-bipyramidal compounds MCl_2(terpy) (M = Zn, Cd).[11] We undertook therefore single-crystal X-ray and spectroscopic studies of the four compounds MCl_3(terpy) (M = Al, Ga, In, Tl). The compounds AlX_3(terpy) (X = Cl, Br), GaX_3(terpy) (X = Cl, Br, I), InX_3(terpy) (X = Br, I) which are described herein have not previously been reported.



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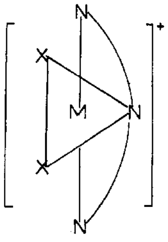

II

Experimental Section

Reagents.—Indium(III) halides were prepared from BDH 99.99% purity indium metal and the anhydrous halogens. Resublimed anhydrous gallium trihalides (99.99% purity) were purchased in sealed ampoules from Fluka, A.G., Buchs, Switzerland. Thallium(III) chloride was prepared by the literature method.[2] Anhydrous, redistilled aluminum halides obtained from Research Inorganic/Organic Chemical Corp., Sun Valley, Calif., were twice sublimed under high vacuum before use. Spectroscopic grade acetonitrile was used in the preparations of indium and thallium complexes. For the aluminum and to a lesser extent the gallium compounds extensive drying of acetonitrile was necessary to obtain satisfactory yields of the anhydrous complexes. Acetonitrile was therefore refluxed over batches of fresh phosphorus pentoxide for 3 days and then fractionated using a 2-in. column packed with helices. Substantial head and tail fractions were discarded.

Preparation of Compounds.—The following synthesis of $AlCl_3$(terpy) is typical of the procedure adopted. Freshly sublimed aluminum trichloride (0.67 g) was dissolved in acetonitrile (35 ml), all manipulations being carried out in a Vacuum Atmospheres Corp. Dri Lab. 2,2,2''-Terpyridyl (1.15 g) in acetonitrile (20 ml) was added and the solution was immediately filtered. On standing overnight in the Dri-Lab, crystals were obtained. These were filtered off, dried under nitrogen, and sealed off in a number of ampoules for subsequent analysis and spectroscopic measurements. $InCl_3$(terpy)[12] and $TlCl_3$(terpy)[2] were prepared as previously described. Microanalyses for new compounds are given in Table I.

TABLE I
ANALYTICAL DATA FOR NEW COMPLEXES

Compound	% C Calcd	% C Found	% H Calcd	% H Found	Color
$AlCl_3(C_{15}H_{11}N_3)$	49.01	48.83	3.26	3.22	Pale yellow
$AlBr_3(C_{15}H_{11}N_3)$	36.03	36.15	2.21	2.45	Pale yellow
$GaCl_3(C_{15}H_{11}N_3)$	43.98	44.09	2.69	2.69	Pale yellow
$GaBr_3(C_{15}H_{11}N_3)$	33.14	33.37	2.23	2.15	Pale yellow
$GaI_3(C_{15}H_{11}N_3)$	26.34	26.48	1.60	1.61	Red
$InBr_3(C_{15}H_{11}N_3)$	30.66	30.42	1.89	1.79	Yellow
$InI_3(C_{15}H_{11}N_3)$	24.73	24.92	1.52	1.64	Bright yellow

Physical Measurements.—Far-infrared spectra were measured as mulls on cesium iodide plates with a Beckman IR 12 spectrometer. For AlX_3(terpy) (X = Cl, Br), samples were prepared under dry nitrogen. Calibrations were carried out with polystyrene and water vapor. Frequencies are accurate to ± 2 cm^{-1}. Raman spectra were recorded on a Cary 81 instrument using He–Ne laser (6328-Å) excitation.

X-Ray Measurements.—Single crystals of the compounds MCl_3(terpy) (M = Al, In, Tl) suitable for X-ray photographic measurements were grown slowly from acetonitrile. A single crystal of $AlCl_3$(terpy) was sealed in a thin-walled glass capillary for X-ray study in view of the hygroscopic nature of this compound. X-Ray photographs were taken on Weissenberg oscillation and Buerger precession cameras using Cu Kα (λ 1.5405 Å) radiation. Densities were measured by flotation, using mixtures of carbon tetrachloride with hexane or tetrabromoethane.

Results and Discussion

Each of the three chloride complexes examined crystallized in the monoclinic system, space group $P2_1/c$ (C_{2h}^5; no. 14), with the systematic absences $h0l$ absent for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ and four molecules per unit cell. Cell dimensions calculated from the precession data are given in Table II, together with comparable data for $GaCl_3$(terpy).[10] The unit cell parameters show an interesting variation in magnitude with increasing atomic weight of the group III metal, there being an overall increase in the axial lengths and a decrease in the β angle from $AlCl_3$(terpy)

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* To whom correspondence should be addressed at the University of Waterloo.

[1] For reviews see (a) R. A. Walton, *Coord. Chem. Rev.*, **6**, 1 (1971); (b) D. G. Tuck, *ibid.*, **1**, 286 (1966); Abstracts, International Colloquium of the National Centre for Scientific Research, Paris, 1970, No. 191, p 159; (c) A. J. Carty, *Coord. Chem. Rev.*, **4**, 29 (1969).

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[12] R. A. Walton, *ibid.*, *A*, 1485 (1967).

TABLE II

CRYSTAL DATA FOR MCl_3(terpy)

Complex	*a*, Å	*b*, Å	*c*, Å	*β*	ρ_c, g cm^{-3}	ρ_m, g cm^{-3}	*U*, Å^3
$AlCl_3$(terpy)	8.346 (18)	14.063 (30)	14.172 (18)	111° 5′	1.569	1.528	1552.0
$GaCl_3$(terpy)[a]	8.324 (3)	14.120 (8)	14.223 (5)	110° 46′	1.725	1.702	1563.1
$InCl_3$(terpy)	8.333 (20)	14.194 (14)	14.268 (20)	109° 40′	1.899	1.825	1589.2
$TlCl_3$(terpy)	8.672 (12)	14.197 (29)	14.412 (28)	108° 17′	2.144	2.157	1684.8

[a] Data taken from ref 10.

TABLE III

FAR-INFRARED AND RAMAN FREQUENCIES OF 2,2′,2′′-TERPYRIDYL COMPLEXES (CM^{-1})[a]

Complex	Spectra	ν(M–X)[b]	ligand	Other bands[f]
$AlCl_3$(terpy)[e]	Ir	470 (20),[b] 355 (20)	426 (16), 301 sh	380 (19), 259 (5), 246 (5), 215 (5)
$AlBr_3$(terpy)[e]	Ir	282 (20)	442 (20), 422 (17)	400 (11), 378 (18), 360 (17), 260 (6), 230 (2)
$GaCl_3$(terpy)	Ir	342 (18), 268 (19)*[c]	419 (9), 322 (12)	220 (20)*
	R	324 (18)	434 (20), 180 (19)	287 (17),* 272 (3)* 257 (12),* 231 (5)
$GaBr_3$(terpy)	Ir	202 (19)	442 (14), 418 (11), 328 (16)	285 sh,* 268 (20),* 247 (7), 215 (19),* 218 (6)
	R	202 (19)	436 (18), 181 (20)	287 (16),* 270 (20),* 252 (13)*
GaI_3(terpy)	Ir	. . .	431 (18), 404 (5)	349 (13), 274 (15),* 227 (20)*
	R	136 (4)	434 (18), 181 (20)	287 (4),* 202 (5)
$InCl_3$(terpy)[d]	Ir	316 (19), 276 (20)	436 (8), 410 (9), 322 sh	356 (2), 250 (11),* 225 (11)*
	R	317 (7)	434 (19), 320 (2), 181 (20)	251 (9),* 240 (10), 227 (16)*
$InBr_3$(terpy)	Ir	. . .	435 (8), 408 (7), 315 (8)	248 (7),* 228 (20),* 202 (15)
	R	172 (20)	434 (18), 320 (4), 181 (20)	287 (14),* 273 (4), 250 (7),* 237 (11), 227 (16),* 126 (14)
InI_3(terpy)	Ir		433 (12), 408 (11), 318 (9)	275 (2), 248 (7),* 228 (6),* 211 (20)*
	R	126 (14)	434 (19), 180 (20)	286 (16),* 272 (3), 250 (17),* 237 (12), 227 (16),* 202 (15), 172 (20)
$TlCl_3$(terpy)[d]	Ir	286 (20), 250 (19)	432 (7), 404 (8), 311 (6)	204 (13)
	R	286 (20), 268 (2)	432 (19), 312 (9)	245 (3), 230 (6), 202 (7), 181 (18)

[a] Figures in parentheses refer to intensities on an arbitrary scale having the strongest band = 20. [b] The occurrence of strong ligand bands in this spectral region makes this assignment tentative. [c] Comparison with the analogous bromide and iodide spectra suggests that this band may arise in part from ν(M–N) and/or a ligand vibration. [d] These spectra are essentially similar to the previously recorded spectra (see ref 12). [e] Only poor-quality Raman spectra were obtained for these compounds owing to fluorescence. [f] Bands marked with an asterisk indicate tentative assignments for ν(M–N).

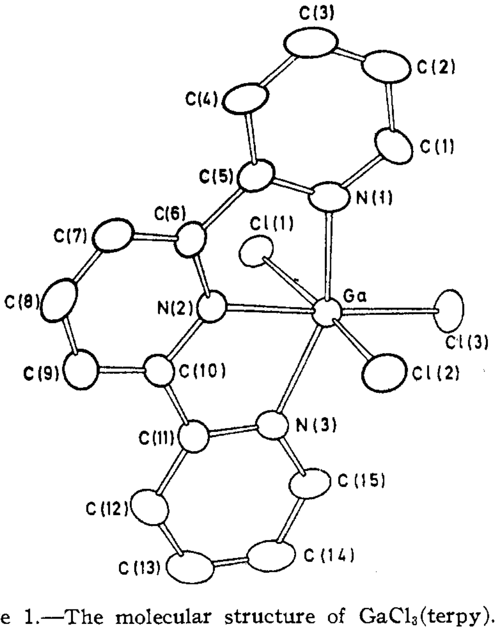

Figure 1.—The molecular structure of $GaCl_3$(terpy). Some pertinent bond angles are as follows: N(1)–Ga–N(2), 77.2 (3)°; N(3)–Ga–N(2), 77.2 (3)°; Cl(1)–Ga–Cl(2), 175.3 (2)°; Cl(1)–Ga–Cl(3), 90.6 (1)°; Cl(2)–Ga–Cl(3), 94.0 (1)°; N(2)–Ga–Cl(3), 174.9 (3)°.

to $TlCl_3$(terpy), although the length of the *a* axis does not differ significantly for $AlCl_3$(terpy), $GaCl_3$(terpy), and $InCl_3$(terpy). The volume of the unit cell thus increases as the metal becomes larger, with the largest change occurring between indium and thallium. These results leave little doubt that the compounds MCl_3(terpy) (M = Al, In, Tl) are isomorphous with one another and with the analogous gallium complex $GaCl_3$(terpy) which has the distorted octahedral trans configuration[10] shown in Figure 1.

In view of the implications of the X-ray results it is interesting to analyze (*post facto*) the infrared and Raman data for the complete series of terpyridyl adducts (Table III) to see whether indeed useful stereochemical information can be extracted for compounds of the *type* MX_3L (L = tridentate ligand) from a simple skeletal analysis.[13] In several cases structural assignments from far-infrared work have not been confirmed by X-ray analysis[14] and the shortcomings of this technique have been emphasized.[6,14]

Although the N(1)–Ga–N(3) angle is less than 180° in $GaCl_3$(terpy),[10] the molecular symmetry approaches C_{2v} (Figure 1).[15] For this structure the skeletal stretching vibrations scan the representation $\Gamma_{str} = 4\ a_1 + 2\ b_2$; each of these modes is both infrared and Raman active. A total of three metal–halogen and three metal–nitrogen modes is therefore expected. A cursory examination of the far-infrared spectra of the series MCl_3(terpy) (M = Al, Ga, In, Tl) and InX_3(terpy) (X = Cl, Br, I) (Figure 2) points out the impossibility of identifying the skeletal modes. Ligand internal modes are, in general, readily followed from complex to complex by comparison with the spectra of the free

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(13) For summaries see (a) D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold, London, 1968; (b) J. R. Ferraro, "Low Frequency Vibrations in Inorganic and Coordination Compounds," Plenum Press, New York, N. Y., 1971.

(14) J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. A*, 2637 (1969).

(15) The atoms N(1), N(2), N(3), Cl(3), and Ga are approximately planar with Cl(1) and Cl(2) trans to this plane.

ligand and other complexes.[16] Also, as an aid to the identification of ν(M–Cl) modes in octahedral compounds the following infrared stretching frequencies may be cited: ν(Ga–Cl) in $GaCl_2(bipy)_2{}^+X^-$, 306 cm^{-1} (X^- = $GaCl_4{}^-$), 304 cm^{-1} (X^- = $PF_6{}^-$);[5] ν(In–Cl) in $InCl_6{}^{3-}$, 250 cm^{-1};[17] ν(In–Cl) in *cis*-$InCl_3(py)_3$ (py = pyridine), 239, 274 cm^{-1};[12] ν(Tl–Cl) in $TlCl_6{}^{3-}$, 230 cm^{-1};[17] ν(Tl–Cl) in $TlCl_3(py)_2$, 268, 253, 224 cm^{-1}.[2] There are no data in the literature for ν(Al–Cl) in octahedral complexes. Authenticated examples of octahedral aluminum complexes containing coordinated halide ion are very rare.[18] However ν_3 for $AlCl_4{}^-$ appears at 496 cm^{-1}.[19] Using the above values as a guide for frequency ranges, two ν(M–Cl) vibrations can be identified with some confidence for MCl_3(terpy) (M = In, Tl) (Table III), but for MCl_3(terpy) (M = Al, Ga) the large frequency separation of the two strong bands assigned to ν(M–Cl) leaves some doubt as to whether the lower band in $GaCl_3$(terpy) and the higher band in $AlCl_3$(terpy) are due to ν(M–Cl), ν(M–N), or a coupled vibration. Moreover, in the series of GaX_3(terpy) (X = Br, I) the far-infrared spectra show a strong band between 260 and 280 cm^{-1} while all three halide complexes exhibit a strong band at 287 cm^{-1} in the Raman. The assignment of ν(Ga–Cl) at 268 cm^{-1} which seemed reasonable from the far-infrared data must therefore be considered tentative. This is typical of the assignment problems with these complexes. Walton[12] in an earlier paper assigned ν(In–Cl) modes at 314 (sh), 305 (s), 270 (s), and 247 cm^{-1} (w, sh) in the far-infrared spectrum of $InCl_3$(terpy). The far-infrared spectra of the series InX_3(terpy) (X = Cl, Br, I) (Figure 2) indicate that only two bands (316, 276 cm^{-1}) are due to ν(In–Cl), since the other bands attributed by Walton to ν(In–Cl) also appear in the spectra of InX_3(terpy) (X = Br, I). The Raman spectra of the indium bromide and iodide complexes show the strong scattering at 287 cm^{-1} apparent in the Raman spectrum of GaX_3(terpy). This band may therefore be due to ν(M–N) or an activated ligand mode. Halogen-insensitive bands appearing between 300 and 200 cm^{-1} may have their origin in ν(M–N) modes. For example the infrared spectra of InX_3(terpy) (X = Cl, Br, I) (Figure 2) exhibit two bands of appreciable intensity at *ca.* 250 and *ca.* 225 cm^{-1} which can be assigned to ν(In–N). In a similar fashion comparison of the spectra of all three gallium derivatives allows the tentative ν(Ga–N) assignments listed in Table III to be made.

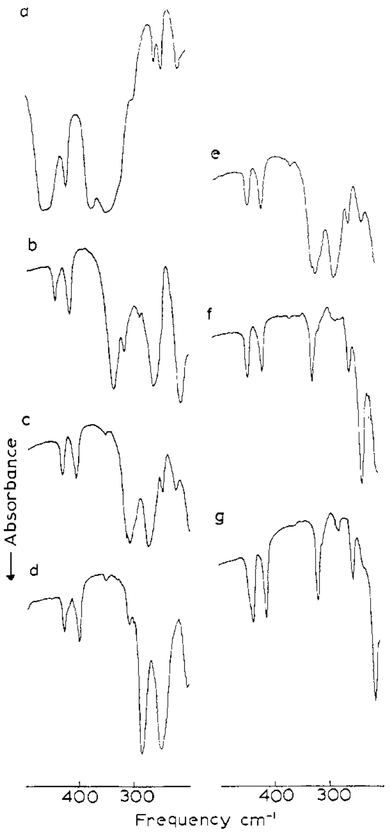

Figure 2.—The far-infrared spectra of (a) $AlCl_3$(terpy), (b) $GaCl_3$(terpy), (c) $InCl_3$(terpy), (d) $TlCl_3$(terpy), (e) $InCl_3$(terpy), (f) $InBr_3$(terpy), and (g) InI_3(terpy).

The crystal structure determination of $GaCl_3$(terpy) indicated that the Ga–Cl bond trans to a terpyridyl nitrogen atom was shorter by 0.13 Å than the average of the remaining two Ga–Cl bond lengths. On this basis the strong band at 342 cm^{-1} is assignable to the symmetric stretching of the Ga–Cl(3) bond. It is of interest to note that for MCl_3(terpy) (M = In, Tl) the highest frequency ν(M–Cl) modes are comparable in frequency to ν_3 of the $MCl_4{}^-$ ions whereas for $GaCl_3$(terpy) the 342-cm^{-1} ν(Ga–Cl) band is 30–40 cm^{-1} lower than ν_3 in $GaCl_4{}^-$.[1c]

The infrared and Raman spectra discussed above for MX_3(terpy) are clearly inadequate as a source of structural information. Although the structures $[M(terpy)_2][MX_6]$ can be readily eliminated,[20] the spectra do not effectively distinguish the formulation trans octahedral MX_3(terpy) from the alternative five-coordinate $[MX_2(terpy)]^+X^-$ for which two ν(M–X) modes are expected at somewhat higher frequencies than ν(M–X) in the complexes MX_2(terpy) (M = Zn, Cd).[21–23] Indeed the far-infrared spectra of MCl_3(terpy) (M = Ga, In) might be interpreted, in the absence of X-ray data, as favoring the latter structure.

The spectroscopic data for MX_3(terpy) contrast shraply with the results reported for *cis*- and *trans*-$RhCl_3(py)_3$[24] where the expected numbers of metal–halogen and metal–nitrogen stretching modes are readily identified. Our results for MX_3(terpy) suggest that the "group vibration" concept of separate metal–halogen and metal–nitrogen vibrations is of limited applicability in complexes with polydentate ligands.

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[19] D. E. H. Jones and J. L. Wood, *Spectrochim. Acta*, **23A** 2695 (1967).

[20] The $AlCl_6{}^{3-}$ and $GaCl_6{}^{3-}$ ions are unknown while the spectra of MCl_3(terpy) (M = In, Tl) (Table III) are not consistent with the known spectra of the hexahalometalate ions.[17]

[21] For $ZnCl_2$(terpy) and $CdCl_2$(terpy) ν(M–Cl) bands have been assigned at 290, 274 and 269, 250 cm^{-1}, respectively.[22,23]

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