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REACTIONS OF BIS(TRIPHENYLGERMYL)CADMIUM WITH PROTIC REAGENTS

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SUMMARY

Reactions of bis(triphenylgermyl)cadmium with water, ethanol, phenol and carboxylic acids occur with heterolytic cleavage of one of the germanium–cadmium bonds. Compounds of the type, $(C_6H_5)_3GeCdOR$ ($R=H$, C_2H_5, C_6H_5, CH_3CO, CF_3CO, C_6H_5CO), are formed as the final or intermediate products. In the latter case they decompose to cadmium and $(C_6H_5)_3GeOR$ compounds or react immediately with protic reagents with scission of the Ge–Cd bond. Some complexes of bis(triphenylgermyl)cadmium, and related compounds, with electron donors were investigated.

INTRODUCTION

In contrast to the well-known $R_3Si{-}HgR'$ and $R_3Ge{-}HgR'$ compounds (R and R' = alkyl), derivatives of the type $R_3Si{-}HgX$ and $R_3Ge{-}HgX$, where X is an electron-withdrawing atom or radical, have been thought to be very unstable and have never been isolated. For example, when X is Cl, Br, I[1-4], CN[3,5], CH_2COOCH_3[1,5] $CH_2COC_2H_5$, C_6F_5[5], $OCOCH_3$[6,7] or $OGe(C_2H_5)_3$[8], these compounds decompose to mercury and R_3SiX (or R_3GeX).

It may be suggested that compounds of the type $(C_2H_5)_3Ge{-}CdOR$ where $R=H$, $n\text{-}C_3H_7$ and CH_3CO are also unstable. It is much more probable that they are the intermediate products in the heterolytic cleavage of bis(triethylgermyl)cadmium with water, propanol or acetic acid[9]. Such reactions occur at ~20° leading to triethylgermane, metallic cadmium and compounds of the type, $(C_2H_5)_3GeOR$:

$$\begin{array}{llr} ROH+[(C_2H_5)_3Ge]_2Cd \xrightarrow{\sim 20^\circ} (C_2H_5)_3GeH+ & (C_2H_5)_3GeCdOR & \\ & \qquad\downarrow & (1) \\ (R=H,\ n\text{-}C_3H_7,\ CH_3CO) & Cd+(C_2H_5)_3GeOR & \end{array}$$

RESULTS AND DISCUSSION

The reaction of bis(triphenylgermyl)cadmium (I) with an excess of water or ethanol *in vacuo* is also adequately described by eq. (1). At ~20° the reactions proceed slowly, but terminate in 2 h at 100° in dioxane. Hydrolysis of this germyl–cadmium compound gave triphenylgermane, cadmium and triphenylgermanol. The latter was isolated in the form of hexaphenyldigermoxane. The reaction with ethanol affords triphenylgermane, cadmium and triphenylethoxygermane.

Equation (1) is also adequate for the reaction of bis(triphenylgermyl)cadmium with phenol. Even with excess of phenol it produces triphenylgermane and phenoxy-(triphenylgermyl)cadmium (II):

$$\underset{}{C_6H_5OH} + \underset{\text{(I)}}{[(C_6H_5)_3Ge]_2Cd} \xrightarrow{100^\circ} (C_6H_5)_3GeH + \underset{\text{(II)}}{(C_6H_5)_3GeCdOC_6H_5} \quad (2)$$

Compound (II) is a colourless air-sensitive crystalline solid, decomposing at 145–150°. It is more stable than compound (I), but with prolonged heating in toluene in an evacuated ampoule at 180° it decomposes to cadmium and triphenylphenoxygermane, *i.e.*, again in accord with Eq. (1)

$$(C_6H_5)_3GeCdOC_6H_5 \xrightarrow{180^\circ} Cd + (C_6H_5)_3GeOC_6H_5 \quad (3)$$

In the reaction of bis(triphenylgermyl)cadmium with acetic and benzoic acids in toluene solution, the composition of the products is dependent on the conditions. At a molar ratio of reagents of 1/1 at room temperature, the heterolytic cleavage concerns one Ge–Cd bond only. The products of acidolysis are triphenylgermane, and acetyloxy(triphenylgermyl)cadmium (III) or benzoyloxy(triphenylgermyl)cadmium (IV), respectively

$$RCOOH + [(C_6H_5)_3Ge]_2Cd \rightarrow (C_6H_5)_3GeH + \underset{\substack{\text{(III), } R = CH_3, \\ \text{(IV), } R = C_6H_5}}{(C_6H_5)_3GeCdOCOR} \quad (4)$$

Compounds (III) and (IV) are colourless air-sensitive crystalline solids. Unlike $(C_2H_5)_3GeCdOCOCH_3$ (see Eq. (1)) they display no tendency to decompose into metallic cadmium and $(C_6H_5)_3GeOCOR$. In (III) and (IV) the Ge–Cd bond is not subject to acidic cleavage at room temperature. For example, instead of the heterolysis of the Ge–Cd bond, the reaction with CH_3COOH leads to the complex, $(C_6H_5)_3$-$GeCdOCOCH_3 \cdot CH_3COOH$ (V).

Acetic acid and bis(triphenylgermyl)cadmium in a 2/1 molar ratio react in toluene solution at room temperature to produce colourless crystals, which also gave the correct analysis for (V):

$$2\,CH_3COOH + [(C_6H_5)_3Ge]_2Cd \rightarrow$$
$$(C_6H_5)_3GeH + \underset{\text{(V)}}{(C_6H_5)_3GeCdOCOCH_3 \cdot CH_3COOH} \quad (5)$$

When acidolysis of bis(triphenylgermyl)cadmium is carried out at 100° in excess of carboxylic acid, the reaction may be satisfactorily described by the following equation:

$$2\,RCOOH + [(C_6H_5)_3Ge]_2Cd \xrightarrow{100^\circ} 2\,(C_6H_5)_3GeH + Cd(OCOR)_2 \quad (6)$$
$$(R = CH_3, CF_3, C_6H_5)$$

Reaction (6) probably involves a step-by-step heterolytic cleavage of the Ge–Cd bonds *via* $(C_6H_5)_3GeCdOCOR$ as an intermediate. In agreement with this suggestion, it was found that the reaction of (III) with acetic acid at 130° gives triphenylgermane and cadmium acetate. It is interesting to note that acidolysis of bis(triethylgermyl)-mercury[7] and bis(triphenylgermyl)mercury[6] requires only 1 mole of acid when the reaction is carried out in excess of acetic acid at 130° (*cf.* Eq. (1)):

$$\begin{array}{ll} CH_3COOH + (R_3Ge)_2Hg \xrightarrow{130^\circ} & R_3GeH + R_3GeHgOCOCH_3 \\ & \qquad\qquad\quad \downarrow \\ (R = C_2H_5, C_6H_5) & \qquad Hg + R_3GeOCOCH_3 \end{array} \tag{7}$$

As reported earlier[10,11], the coordinative saturation of cadmium increased the stability of organometallic compounds containing the metal–cadmium bond (*e.g.*, $(C_6H_5)_3SnCdCl$ and $(C_6H_5)_3SnCdSn(C_6H_5)_3$ compounds).

In compound (II) the coordinatively unsaturated cadmium is bonded with an oxygen atom containing free electron pairs. As a rule, similar compounds are generally associated. For example, the organocadmium compounds of type CH_3CdOR (R = hydrocarbon moiety) are known to give cyclic associates stable in benzene[12]. The cryoscopic molecular weight measurement, however, shows that compound (II) is a monomer in benzene solution. Hence, in this case cadmium coordinative saturation does not take place.

It may thus be assumed that the stability of compound (II) increases owing to the oxygen unshared electron pair density shifting to the vacant orbitals of cadmium: $(C_6H_5)_3GeCd \Leftarrow OC_6H_5$. Clear evidence of this effect was found for such compounds as $(CH_3)_3SiOAr$[13] where Ar = aryl.

Attempts to measure the molecular weight of (III) and (IV) by cryoscopy were unsuccessful because of their low solubility in solvents, from which we assume that these compounds have polymeric structures. Cyclic associates are not excluded for such compounds[14]. Complex (V) formation from (III) shows that in the latter the cadmium atom is coordinatively unsaturated.

We found that complex (V) and methylmagnesium iodide react with quantitative evolution of methane. The infrared spectrum of (V) shows carbonyl stretching bands at 1547 and 1680 cm^{-1}. These values differ from those found in $Cd(OCOCH_3)_2$ (1560 cm^{-1}) and in CH_3COOH (1760 cm^{-1}). Hence, coordination of oxygen to the metal should result in a lowering of the carbonyl stretching frequencies in complex (V) compared with those in the free ligands.

Bis(triphenylgermyl)cadmium is in a monomeric form in benzene. It reacts with pyridine, piperidine, diethylamine, triphenylphosphine, tetrahydrofuran and dioxane to give the complexes (Table 1) with three- or tetra-coordinate cadmium. Unlike the initial bis(triphenylgermyl)cadmium, they are fairly stable.

A recent study[16] shows that compounds $[\pi\text{-}C_5H_5M(CO)_3]_2Cd$ (M = Mo or W) give stable complexes with mono- and bi-dentate amines while only weak adducts were shown to exist with ligands coordinated *via* oxygen. Bis(triphenylgermyl)cadmium forms stable complexes with both types of ligands.

Finally, in the reaction of bis(triethylsilyl)cadmium with diethylamine, decomposition of the intermediate product, $(C_2H_5)_3SiCdN(C_2H_5)_2$, was found to take place:

$$(C_2H_5)_2NH + [(C_2H_5)_3Si]_2Cd \rightarrow (C_2H_5)_3SiH + Cd + (C_2H_5)_3SiN(C_2H_5)_2 \tag{8}$$

TABLE 1

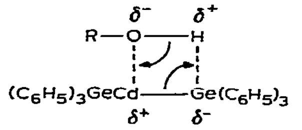
YIELDS, PROPERTIES AND ANALYSES OF COMPLEXES CONTAINING Ge–Cd BONDS

No.	Complex	Yield (%)	M.p. (°C)	Found (%)			Calcd. (%)		
				C	H	Cd	C	H	Cd
V	$(C_6H_5)_3GeCdOCOCH_3 \cdot CH_3COOH$	74.9	162 dec.	49.47	4.22	20.70	49.35	4.14	20.99
VI	$[(C_6H_5)_3Ge]_2Cd \cdot (C_2H_5)_2NH$	81.2	130 dec.	–	–	13.78	–	–	14.15
VIII	$[(C_6H_5)_3Ge]_2Cd \cdot 2\ C_5H_5N$	85.9	128	62.73	4.58	12.40	62.89	4.59	12.79
IX	$[(C_6H_5)_3Ge]_2Cd \cdot 2\ C_4H_8O$	60.0	100	61.19	5.61	13.15	61.13	5.36	13.05
X	$[(C_6H_5)_3Ge]_2Cd \cdot 2$ dioxane	61.2	165 dec.	58.42	5.21	13.33	58.95	5.17	12.54
XI	$[(C_6H_5)_3Ge]_2Cd \cdot 2\ (C_6H_5)_3P$	69.4	245–250 dec.	71.00	5.58	8.65	69.47	4.86	9.03
XII	$[(C_6H_5)_3Ge]_2Cd \cdot$ piperidine	72.2	102	60.98	5.32	13.45	61.14	5.13	13.95
XIII	$(C_6H_5)_3Ge\ CdOC_6H_5 \cdot C_5H_5N$	76.4	165 dec.	59.51	4.49	19.10	59.18	4.28	19.10

In contrast, bis(triphenylgermyl)cadmium reacts with diethylamine to give a good yield of complex (VI), $[(C_6H_5)_3Ge]_2Cd \cdot (C_2H_5)_2NH$, which can be decomposed in toluene at 170° to triphenylgermane, cadmium and triphenyl(diethylamino)germane:

$$\underset{(VI)}{[(C_6H_5)_3Ge]_2Cd \cdot (C_2H_5)_2NH} \rightarrow (C_6H_5)_3GeH + Cd + (C_6H_5)_3GeN(C_2H_5)_2 \qquad (9)$$

It may thus be assumed that coordination of protic reagents to cadmium is needed for the cleavage of bis(triphenylgermyl)cadmium. Subsequent selective fission of the Ge–Cd bond involves the four-centre transition state (VII) in accord with the S_E1 mechanism.



(VII)

Such a transition state is characterized by a nucleophilic attack at cadmium along with an electrophilic attack at the germanium atom. The compounds generated, $(C_6H_5)_3GeCdOR$ (R = H, alkyl, phenyl, CH_3CO, CF_3CO, C_6H_5CO), decompose or undergo a subsequent protolytic fission along the Ge–Cd bond.

EXPERIMENTAL

All reactions were carried out in evacuated sealed ampoules. Reagents and solvents were degassed before use. Melting point of compounds containing the Ge–Cd bond were determined using sealed evacuated tubes.

Hydrolysis of bis(triphenylgermyl)cadmium (I)

A solution of 2 ml of water in 8 ml of dioxane was added to 2.65 g (0.0037 mole) of (I). Cadmium was slowly precipitated. The mixture was heated for 2 h at 100°. The organic layer was decanted from the cadmium and the solvent evaporated *in vacuo*. The residue was extracted with cold hexane. The remaining insoluble material was recrystallized from a toluene–hexane mixture. The yield of hexaphenyldigermoxane was 0.75 g (65.2%), m.p. and mixed m.p., 180°. The hexane extract was distilled. 0.80 g (71.4%) of triphenylgermane was obtained, b.p. 151–152° (1 mm); m.p. and mixed m.p., 46°. Cadmium was washed with ether, dissolved in HNO_3 and analyzed by titration. Yield 0.40 g (97.5%).

Reaction of (I) with ethanol

A mixture of 2.60 g (0.0036 mole) of (I) and 5 ml of absolute ethanol was heated at 100° for 3 h; 0.40 g (98.6%) of cadmium was precipitated. Ethanol was removed *in vacuo*. The residue was dissolved in a small amount of boiling hexane and filtered. 0.65 g (51.6%) of triphenylethoxygermane crystallized on cooling; m.p. 85° (mixed m.p.). (lit.[17] m.p. 86–87°).

Distillation of the mother liquor gave 0.90 g (81.6%) of triphenylgermane, b.p. 155–157° (1.5 mm); m.p. 44–45°.

Reaction of (I) with phenol

A mixture of 2.00 g (0.0028 mole) of (I), 0.80 g (0.0085 mole) of phenol and 10 ml of toluene was heated for 2 h at 100°. No cadmium precipitated. Volatiles were removed by recondensation *in vacuo*. The residue was extracted with hexane. 1.34 g (94.6%) of phenoxy(triphenylgermyl)cadmium (II) was obtained by the usual procedure, m.p. 145–150° (decomp.), colourless plates, insoluble in hexane, slightly soluble in benzene and toluene, (Found: Cd, 21.84%; mol. wt. 509. $C_{24}H_{20}CdGeO$ calcd.: Cd 22.06%; mol. wt. 509). Distillation of the hexane extract gave 0.51 g (60.3%) of triphenylgermane with m.p. 44–45°.

A mixture of 0.61 g (0.0012 mole) of (II) and 5 ml of toluene was heated at 180° for 5 h in evacuated ampoule. 0.12 g (88.9%) of cadmium precipitated. The toluene was evaporated. Recrystallisation of the residue from a toluene–hexane mixture afforded 0.38 g (80.0%) of triphenylphenoxygermane with m.p. 94°. (Found: C, 71.84; H, 5.20. $C_{24}H_{20}GeO$ calcd.: C, 72.61; H, 5.08%.)

Reaction of phenoxy(triphenylgermyl)cadmium (II) with acetic acid

A solution of 2.75 g (0.0054 mole) of (II) in 15 ml of toluene was added to 1.29 g (0.0216 mole) of glacial acetic acid at room temperature. During the addition, the complex, $(C_6H_5)_3GeCdOCOCH_3 \cdot CH_3COOH$ (V), precipitated. It was filtered off, washed with toluene and dried *in vacuo*. The yield was 2.50 g (86.6%), m.p. 162° (decomp.). The complex was sparingly soluble in hexane, benzene and toluene. (Found: C, 49.47; H, 4.22; Cd, 20.70; CH_3COO, 22.00. $C_{22}H_{22}CdGeO_4$ calcd.: C, 49.35; H, 4.14; Cd, 20.99; CH_3COO, 22.06%.)

Analysis of the original filtrate and toluene extract gave 0.39 g (77.1%) of phenol (*via* 2,4,6-tribromophenol).

Reaction of (I) with acetic acid

(*a*) *Molar ratio* 1/1. A mixture of 2.70 g (0.0037 mole) of (I), 0.25 g (0.0037 mole) of glacial acetic acid and 20 ml of toluene was heated at 100° until complete decolourisation of the solution (2 h). The solvent was removed *in vacuo*, and the residue extracted with hexane. 1.14 g (97.6%) of triphenylgermane was isolated from the extract by the usual procedure. The colourless crystalline solid, insoluble in hexane, was dried *in vacuo*; 1.43 g (78.4%) of acetyloxy(triphenylgermyl)cadmium (III) was obtained, m.p. 145–150° (decomp.). The compound was sparingly soluble in hexane, benzene and toluene. (Found: Cd, 23.40. $C_{20}H_{18}CdGeO_2$ calcd.: Cd, 23.66%.)

0.30 g (0.0024 mole) of acetic acid was added to a mixture of 1.15 g (0.005 mole) of (III) and 10 ml of toluene. The mixture was allowed to stand overnight at room temperature. The solvent was decanted from the solid, the latter washed with hexane and dried *in vacuo*. 0.97 g (74.9%) of complex (V) was obtained, m.p. and mixed m.p. 162° (decomp.) (Found: Cd, 20.65; CH_3COO, 22.10. $C_{22}H_{22}CdGeO_4$ calcd.: Cd, 20.99; CH_3COO, 22.06%.)

(*b*) *Molar ratio* 1/2. A mixture of 3.10 g (0.0043 mole) of (I), 0.52 g (0.0086 mole) of acetic acid and 20 ml of toluene was allowed to stand at room temperature for 24 h. A colourless crystalline solid precipitated. A workup in the usual manner afforded 1.72 g (74.6%) of (V), m.p. 160° (decomp.). (Found: CH_3COO, 22.16. $C_{22}H_{22}CdGeO_4$ calcd.: CH_3COO, 22.06%.) 1.24 g (94.6%) of triphenylgermane was isolated from the filtrate by the usual procedure, m.p. 45–46°

(*c*). A mixture of 2.50 g (0.0035 mole) of (I) and 10 ml of acetic acid was heated at 100° for 5 h. The usual purification procedure gave 0.71 g (88.8%) of cadmium acetate, m.p. 252–254° (mixed m.p.) and 1.60 g (75.6%) of triphenylgermane with m.p. 44–45°.

Reaction of acetyloxy(triphenylgermyl)cadmium (III) with acetic acid

A mixture of 1.31 g (0.0027 mole) of (III), 2.00 g (0.0333 mole) of acetic acid and 10 ml of toluene was heated at 130° for 2 h. A crystalline solid slowly precipitated from the initial homogeneous solution. 0.57 g (67.9%) of triphenylgermane and 0.53 g (88.4%) of cadmium acetate were isolated from the reaction mixture by the procedure described above.

Reaction of (I) with benzoic acid

(*a*) *Molar ratio* 1 : 1. 2.20 g (0.0030 mole) of (I) in 15 ml of toluene was added to solution of 0.37 g (0.0030 mole) of benzoic acid in 10 ml of the same solvent. The mixture was allowed to stand overnight at room temperature. The liquid phase was decanted from the crystalline solid. The latter was washed with hexane and dried. The yield of benzoyloxy(triphenylgermyl)cadmium (IV) was 1.60 g (97.5%), m.p. ~150° (decomp.) The compound is sparingly soluble in hexane, benzene and toluene. (Found: Cd, 20.85. $C_{25}H_{20}CdGeO_2$ calcd.: Cd, 20.94%.) The liquid phase and the hexane extract were distilled. 0.72 g (82.6%) of triphenylgermane was obtained, b.p. 161–164° (2 mm), m.p. 43–45°.

(*b*). A mixture of 2.00 g (0.0028 mole) of (I), 1.00 g (0.0082 mole) of benzoic acid and 10 ml of toluene was heated at 100° for 2 h. The colourless solid precipitated was filtered off, washed with toluene and dried *in vacuo*. 0.72 g (79.2%) of cadmium benzoate was obtained. (Found: Cd, 31.98. $C_{14}H_{10}CdGeO_4$ calcd.: Cd, 31.69%.) The filtrate was distilled. The yield of triphenylgermane was 1.22 g (72.1%), m.p. 44–45°

Reaction of (I) with excess trifluoroacetic acid

A mixture of 2.60 g (0.0036 mole) of (I), 1.50 g (0.0131 mole) of trifluoroacetic acid and 10 ml of toluene was heated at 90° for 3 h. The reaction mixture was worked up as usual to give 1.45 g (66.3%) of triphenylgermane and 1.04 g (85.2%) of cadmium trifluoroacetate as colourless crystals deteriorating in air. (Found: Cd, 32.40. $C_4CdF_6O_4$ calcd.: Cd, 33.21%.)

Preparation of complexes of (I)

(a) A mixture of 2.80 g (0.0039 mole) of (I), 1.50 g (0.0205 mole) of diethylamine and 15 ml of toluene was heated for 5 h at 100°. No cadmium precipitated. Evaporation of the solvent and subsequent recrystallisation of the remaining solid from a toluene–hexane mixture yielded 2.50 g (81.2%) of the complex $[(C_6H_5)_3Ge]_2Cd\cdot(C_2H_5)_2NH$ (VI).

An analogous procedure gave complex (VIII) (Table 1).

(b) A solution of 1.50 g (0.0021 mole) of (I) in 10 ml of toluene was added to 5 ml of tetrahydrofuran cooled in a liquid nitrogen bath. The characteristic greenish colour of (I) disappeared on heating the mixture to room temperature. The solution was allowed to crystallize overnight at ~ 10°. Filtration and vacuum drying yielded 1.08 g (60.0%) of complex (IX) (Table 1).

The complexes (X, XI, XII, XIII) were prepared analogously.

Decomposition of complex (VI)

2.50 g (0.0029 mole) of complex (VI) was heated in 10 ml of toluene for 14 h at 180° in a sealed ampoule. The organic layer was decanted from the cadmium (0.34 g, 96.1%); the solvent was evaporated *in vacuo*. The residue was recrystallized from hexane. The yield of triphenyl(diethylamino)germane was 0.76 g (64.2%), m.p. 176°. (Found: C, 70.50; H, 6.23. $C_{22}H_{25}GeN$ calcd.: C, 70.27; H, 6.72%.) 0.75 g (78.1%) of triphenylgermane was isolated from the mother liquor by the usual procedure, m.p. 43–44°.

REFERENCES

1 N. S. Vyazankin, E. N. Gladyshev, E. A. Arkhangel'skaya and G. A. Razuvaev, *J. Organometal. Chem.*, 17 (1969) 340.
2 N. S. Vyazankin, E. N. Gladyshev, E. A. Fedorova and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 186 (1969) 1082.
3 A. G. Lee, *J. Organometal. Chem.*, 16 (1969) 321.
4 D. Seyferth, R. J. Cross and B. Prokai, *J. Organometal. Chem.*, 7 (1967) P20.
5 O. A. Kruglaya, B. I. Petrov and N. S. Vyazankin, *Zh. Obshch. Khim.*, in press.
6 N. S. Vyazankin, V. T. Bychkov, O. V. Linzina and G. A. Razuvaev, *Zh. Obshch. Khim.*, 39 (1969) 979.
7 O. A. Kruglaya, N. S. Vyazankin and G. A. Razuvaev, *Zh. Obshch. Khim.*, 35 (1965) 394.
8 G. A. Razuvaev, Yu. A. Alexandrov, V. N. Glushakova and G. N. Figurova, *J. Organometal. Chem.*, 14 (1968) 339.
9 N. S. Vyazankin, G. A. Razuvaev and V. T. Bychkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1965) 1665.
10 H. M. J. C. Creemers, *Hydrostannolysis. A General Method for Establishing Tin–Metal Bonds*, Schotanus and Jens, Utrecht, 1967.
11 F. J. A. Des Tombe, G. J. M. van der Kerk, H. M. J. C. Creemers and J. G. Noltes, *Chem. Commun.*, (1966) 914.
12 G. E. Coates and A. Lauder, *J. Chem. Soc., A*, (1966) 264.
13 H. Bock and H. Alt, *Chem. Commun.*, (1967) 1299.
14 G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, (1964) 1295.
15 W. West (Ed.), *Chemical Applications of Spectroscopy*, Interscience, New York, 1956.
16 M. J. Mays and J. D. Robb, *J. Chem. Soc., A*, (1969) 561.
17 K. A. Hooton and A. L. Allred, *Inorg. Chem.*, 4 (1965) 671.