661. Beryllium Complexes with Bipyridyl and Other Chelate Donor Groups: Evidence for the Bipyridyl Anion as Donor.

By G. E. Coates and S. I. E. Green.

Dimethylberyllium forms monomeric 1 : 1 complexes with the chelating donors 1,2-dimethoxyethane and *NNN'N'*-tetramethylethylenediamine. *NNN'*-Trimethylethylenediamine yields a dimer $(Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NMe{\cdot}BeMe)_2$, and the dimethylethylenediamines give polymers.

Dialkyl and diaryl derivatives of beryllium form coloured 2,2'-bipyridyl complexes [R_2 bipy Be], whose colours deepen as the group R becomes less electronegative. The colour is ascribed to a charge-transfer transition from a Be–C bond to the bipyridyl group. Organic derivatives of some other Group II metals give coloured bipyridyl complexes, *e.g.*, [Me_2 bipy Zn].

Reaction between Li_2 bipy and [Cl_2 bipy Be] or between Li bipy and beryllium chloride gives a deep green paramagnetic complex [$bipy_2$ Be], which is regarded as a complex between two bipyridyl monoanions and the beryllium cation. The complex Li[$bipy_2$ Be], deep violet-blue in ether solution, was also prepared.

Benzene-soluble sulphide complexes of beryllium chloride, $[Cl_2(Me_2S)_2Be]$, $[Cl(Me_2S)BeCl_2Be(Me_2S)Cl]$, and $[Cl_2(MeSC_2H_4SMe)Be]$, are also described.

DIMETHYLBERYLLIUM forms a 1 : 1 complex with trimethylamine which does not noticeably dissociate up to 180°, and an unstable 2 : 3 complex $(Me_2Be)_2(NMe_3)_3$ which readily loses a mol. of trimethylamine.[1] Our inability to prepare the bisamine complex $Me_2Be(NMe_3)_2$ was surprising, particularly since we obtained an unstable bisphosphine complex $Me_2Be(PMe_3)_2$. The non-formation of $Me_2Be(NMe_3)_2$ must be due to an entropy rather than a steric effect, since we have now been able to prepare a complex (I) with

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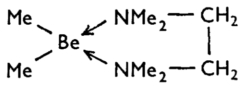
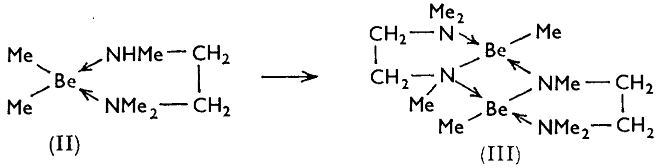
[1] Coates and Huck, *J.*, 1952, 4501.

NNN'N'-tetramethylethylenediamine. This compound is about 10% associated in benzene solution; some association would be expected since a compound (I) no doubt has a large dipole moment.

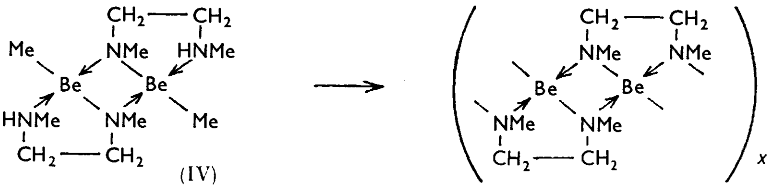
In contrast to dimethyl and diethyl ether which form unstable complexes with high dissociation pressures at room temperature, the chelating diether 1,2-dimethoxyethane forms a well-defined complex $Me_2Be(MeO{\cdot}C_2H_4{\cdot}OMe)$, m. p. 100—101°, which may be crystallized from diethyl ether. It is, however, more reactive to the atmosphere than the diamine complex (I). It is monomeric in benzene and its dissociation pressure must be very small since it sublimes unchanged at 60—70°/0·06 mm.


(I)


(II) (III)

Since the dimethylamine complex, $Me_2Be,NHMe_2$, loses a mol. of methane when it is melted (44°) and forms a trimer[2] $(MeBeNMe_2)_3$, the dimethylberyllium complexes of ethylenediamines containing reactive amino-hydrogen should yield products in which co-ordinative unsaturation of the beryllium is relieved by association or polymerization. *NNN'*-Trimethylethylenediamine forms a complex (II) which loses a mol. of methane at room temperature forming a dimer (III).

Ethylenediamines with two or more amino-hydrogen atoms give polymeric products, though intermediates containing two beryllium atoms were isolated in reactions with both symmetrical and unsymmetrical dimethylethylenediamine. Methane (1 mol.) is evolved from a frozen mixture of *NN'*-dimethylethylenediamine and dimethylberyllium in ether, as soon as the reactants melt. The product (IV) sublimes slowly in a vacuum from 90°, and at 145° suddenly decomposes, with evolution as methane of four-fifths of the remaining methyl bound to beryllium. Freezing of the resulting polymer (V) could account for a proportion of Me–Be groups not reacting with NH groups. If the dimer (IV) is heated in tetralin solution, methane is evolved from 140° to 150° and eventually a clear gel results, from which, after removal of tetralin, acid releases no methane. The polymer (V) is insoluble in all the common organic solvents, but reacts rapidly and exothermally with water to form beryllium hydroxide and regenerate the diamine.


(IV) (V)

The unsymmetrical diamine $(Me_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)$ behaves in a more complex way. Evolution of one mol. of methane gives a product analogous to (IV); this sublimes slowly in a vacuum from 115° and gradually evolves more methane from 138°. At 170° it melts with vigorous evolution of methane, then partly solidifies, forming colourless needles. This transient reaction intermediate melts almost immediately with further effervescence, giving a viscous liquid which sets to a glass when cooled.

Ethylenediamine itself liberates about 80% of the methyl from dimethylberyllium at room temperature, with formation of a white amorphous evidently polymeric material. Some methyl groups (about 6%) are retained even after heating, and are released on reaction with water or aqueous acids.

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[2] Coates, Glockling, and Huck, *J.*, 1952, 4512.

2,2′-Bipyridyl Complexes.—Addition of bipyridyl to an ether solution of dimethylberyllium gives an immediate golden-yellow crystalline precipitate of Me_2(bipy)Be. Similar complexes with unexpected colours are formed by some other beryllium compounds,[3] and are listed in the Table, in which only the long-wavelength absorption

X in X_2 bipy Be	Colour	$\lambda_{max.}$ (mμ)	Molar extinction coefficient, $\times 10^{-3}$
Cl	White	352 infl.	1·2
Br	Pale cream	364	2·4
I	Yellow	368	7·0
Ph	Yellow	353 infl.	0·5
Me	Yellow	395	2·7
Et	Red	461	3·7

absorption band is given. All the complexes have high-intensity bands in the 220—300 mμ region, similar to those of free bipyridyl (see Figs. 1 and 2). For the absorptions causing visible colour, Fig. 1 shows a small decrease in $\lambda_{max.}$ and a marked decrease in extinction coefficient in passing from the less to the more electronegative halogen. In the case of the organo-complexes (Fig. 2) both $\lambda_{max.}$ and extinction coefficients decrease as the electronegative character of the organic group increases. Deep red colours were obtained when bipyridyl was added to ether solutions of di-n-butyl- and di-isopropyl-beryllium, but the resulting complexes gradually decomposed. Similarly addition of *p*-dimethylaminophenyl-lithium, followed by bipyridyl, to ethereal beryllium chloride gave an orange complex, but this gradually deposited tar and we were unable to purify it satisfactorily.

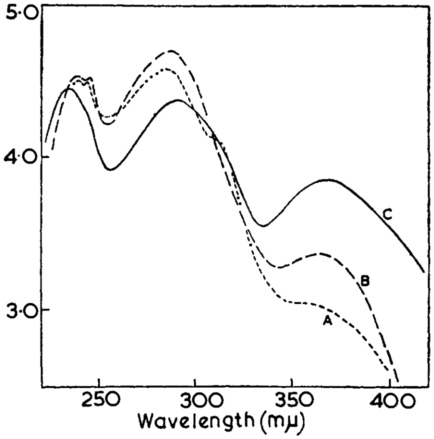

FIG. 1. Absorption spectra of beryllium halide bipyridyl complexes.

A, bipy $BeCl_2$; B, bipy $BeBr_2$; C, bipy BeI_2.

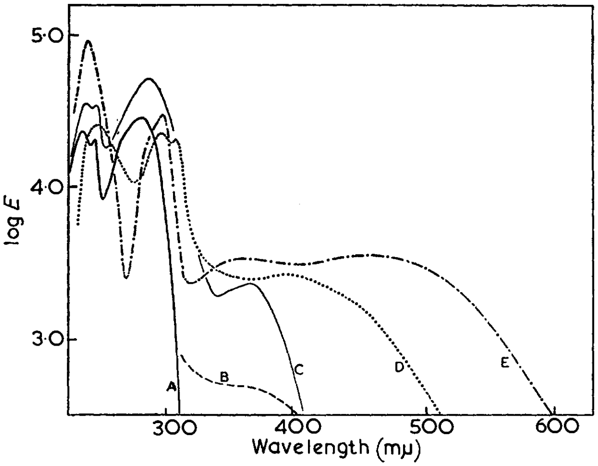

FIG. 2. Absorption spectra of organo-beryllium bipyridyl complexes.

A, Bipyridyl; B, bipy $BePh_2$; C, bipy $BeBr_2$; D, bipy $BeMe_2$; E, bipy $BeEt_2$.

These observations support the suggestion that the colours are due to electron-transfer from one of the Be–X bonds to the lowest unoccupied orbital of the bipyridyl. In the excited state of the complex the Be–X bonds would thus be acting as electron-donors, and their donor character would clearly be greater if the electrons in the bonds were relatively loosely held, as is probable in the Be–alkyl bond, than if the bonding were strong as it probably is in the Be–Cl bond. A decrease in the electronegativity of X should increase the extinction coefficient, as observed, since it would increase the size of the beryllium orbitals and hence the extent of their overlap with the π-orbitals of the bipyridyl. The effect is essentially similar to the back-donation well known in carbonyl, phosphine,

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[3] Coates and Green, *Proc. Chem. Soc.*, 1961, 376.

and bipyridyl complexes of transition metals, only in the case of the beryllium complexes the absorption of a quantum of light (about 64—80 kcal. mole^{-1}) is necessary. If we assume that in the excited state a beryllium–carbon bond has become a one-electron or half bond, chemical decomposition would not necessarily result. In the dimethylberyllium polymer all the beryllium–carbon bonds are half bonds.

It is possible that in the halide complexes the electron source is one of the non-bonding orbitals of the halogen atom, but in the organo-complexes the Be–C bond seems the only electron source. For example, in the dimethyl complex the only other bonds are methyl C–H bonds.

Similar electronic transitions have been suggested as the origin of the colours of a number of decaborane derivatives. For example, the introduction of electron-attracting substituents in the pyridine rings of $B_{10}H_{12}\ py_2$ complexes deepens their colours.[4]

Diethylberyllium forms a dipyridine complex, $Et_2\ py_2\ Be$, orange-yellow in colour and monomeric in benzene solution like its red bipyridyl analogue. Pyridine appears to act as a stronger donor than trimethylamine towards diethylberyllium, since the latter forms only a monoamine complex [5] $Et_2(Me_3N)Be$; if more than one mol. of amine co-ordinates it can be removed by pumping at —40°. Dimethylberyllium gives a colourless dipyridine complex which melts to a yellow liquid, in contrast to the bright yellow Me_2 bipy Be.

Coloured complexes with bipyridyl are formed by organic derivatives of some other Group II elements. Organomagnesium compounds are very reactive and Grignard reagents add to pyridine giving, for example, 2-arylpyridines. However, addition of bipyridyl to an ether solution of diethylmagnesium results in a deep red solution very similar in appearance to that obtained from $Bu^n{}_2Be$ and bipyridyl. In both instances rapid removal of solvent gives a dark red tar which becomes brown in a few hours. Bipyridyl and diphenylmagnesium give an immediate orange-yellow precipitate, which becomes chocolate-brown in about ten minutes at room temperature.

The less reactive dimethyl derivatives of the Group IIB elements form an interesting sequence in their behaviour with bipyridyl. Dimethylzinc forms a bright yellow complex Me_2 bipy Zn, from which dimethylzinc cannot be removed by pumping (at room temperature). Dimethylcadmium forms an unstable yellow complex, which has an appreciable dissociation pressure at room temperature since prolonged pumping leaves only colourless bipyridyl. Dimethylmercury dissolves bipyridyl without colour change and can rapidly be recovered by pumping at room temperature.

The zinc complex Me_2 bipy Zn is remarkably unreactive, being decomposed (becoming white) only after exposure to the air for several hours. The *o*-phenanthroline complex, Me_2 phenan Zn, is similar in appearance and properties. As expected by analogy with the beryllium compounds, Et_2 bipy Zn has a deeper colour (orange-red) than the dimethyl complex; it is also much more rapidly decomposed in the air. The only dialkylzinc complexes previously described are the unstable tetrahydrofuran complex [6] $(Me_2Zn)_2(C_4H_8O)_3$ and the anionic complexes exemplified by Li_2ZnMe_4,Et_2O.[7]

Bipyridyl Anion Complexes.—Bipyridyl in ether solution reacts with lithium, forming a deep red solution containing the lithium salt of the bipyridyl anion. In tetrahydrofuran further reaction gives the deep green dilithium derivative, and these reagents have been used in the preparation of bipyridyl compounds of titanium(0) and of titanium(—1),[8] *viz.*, $bipy_3$ Ti and Li[$bipy_3$ Ti]. When an ether solution of bipyridyl-lithium is added to beryllium chloride, also in ether, the deep red colour at once changes to an intense green and lithium chloride is precipitated:

$$2Li^+bipy^- + BeCl_2 = [bipy_2\,Be] + 2LiCl\downarrow$$

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[4] Graybill and Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 2673.

[5] Personal communication from Mr. N. A. Bell.

[6] Thiele, *Angew. Chem.*, 1959, **71**, 650.

[7] Hurd, *J. Org. Chem.*, 1948, **13**, 711.

[8] Herzog and Taube, *Z. anorg. Chem.*, 1960, **306**, 159.

The same product is obtained when the dilithium derivative of bipyridyl is added to a suspension of dichloro(bipyridyl)beryllium in tetrahydrofuran or in 1,2-dimethoxyethane. In this case there is no striking colour change but the very sparingly soluble [Cl_2 bipy Be] dissolves readily when the [Li_2 bipy] is added:

$$\text{Li}_2\text{ bipy} + [\text{Cl}_2\text{ bipy Be}] = [\text{bipy}_2\text{ Be}] + 2\text{LiCl}$$

The compound [$bipy_2$ Be], whose colour is due to the tail of a very intense broad absorption band ($\lambda_{max.}$ 801 mμ; there is another band with a maximum at 899 mμ), could be formulated as a bipyridyl complex of beryllium(0) in which the beryllium would presumably have two electrons in the 2*s* level, or as a bis(bipyridyl$^-$) complex of the beryllium(II) cation. Professor R. S. Nyholm and Dr. C. S. Pande, of University College, London, kindly measured the magnetic susceptibility of this compound and found values of 2·05 and 2·15 B.M. for the room-temperature susceptibilities of two specimens after diamagnetic corrections had been made. Though the formulation [$(bipy^-)_2Be^{2+}$] would imply a susceptibility of 2·8—2·9 B.M., the rather lower observed paramagnetism excludes the formulation as a beryllium(0) complex since this should be diamagnetic. The difference between the observed susceptibility and that expected for a complex containing two bipyridyl anions, each with a single electron in its non-degenerate[9] highest occupied orbital, could be due to at least two possible effects. In the first place some decomposition into diamagnetic products could have occurred in the interval between the preparation of the compound in Durham and the magnetic measurements in London. Alternatively there may be an equilibrium with the diamagnetic complex [$(bipyridyl^{2-})bipyridyl^0Be^{2+}$]. We think we have eliminated the first possibility by cooling the specimens to —78° (or lower) immediately after they were prepared and sealed in the Gouy tubes, and keeping them at a low temperature until immediately before their magnetism was measured. Further, there was insignificant change in magnetism after the specimens had remained two weeks at room temperature.

An equilibrium such as [$(bipyridyl^-)_2Be^{2+}$] $\rightleftharpoons$ [$(bipyridyl^{2-})(bipyridyl^0)Be^{2+}$] would very probably be temperature-dependent, but at present we have no opportunity to explore the variation of magnetic properties with temperature.

If an ether solution of bisbipyridylberyllium is stirred with an excess of lithium metal, the deep green colour changes through brown to a deep violet. A black product, Li[$bipy_2$ Be], can be isolated from the reaction mixture. The properties of this compound have not been studied in detail, but Professor Nyholm and Dr. Pande report that it is weakly paramagnetic.

These beryllium complexes evidently differ from the bipyridyl complexes of transition metals in low valency states, *e.g.*, [$bipy_3$ Ti][8] and [$bipy_3$ V].[10] The transition-metal compounds are regarded as complexes of neutral bipyridyl with the metals in their zero oxidation level. The different formulation of the beryllium compounds as derivatives of the bipyridyl anion is supported, not only by magnetic evidence, but also by their very deep colours; compare the intense colours of hydrocarbon anions.

Incidentally to this investigation, some complexes of beryllium chloride with tetrahydrofuran, 1,2-dimethoxyethane, dimethyl sulphide, and 1,2-dimethylthioethane were prepared. While this work was in progress the tetrahydrofuran and 1,2-dimethoxyethane complexes were described elsewhere,[11] and the others are described below.

EXPERIMENTAL

M. p.s are corrected. Organoberyllium complexes were handled in a vacuum-apparatus, or apparatus attached thereto, which incorporated a Töpler-type pump and burette for the measurement of gas (methane) not condensed by liquid air. Most of the compounds were very

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[9] Orgel, *J.*, 1961, 3683.

[10] Herzog, *Z. anorg. Chem.*, 1958, **294**, 156.

[11] Turova, Novoselova, and Semenenko, *Russ. J. Inorg. Chem.*, 1959, **4**, 1104; 1960, **5**, 828.

sensitive to moisture and were analyzed by transferring a sample to a weighed flask in a dry-box, followed by hydrolysis on the vacuum-line and, in some instances, analysis for beryllium in the residue (ignition with pumice of precipitated beryllium hydroxide). Aliphatic diamines were dried with sodium or potassium, and then distilled; bipyridyl was sublimed in a vacuum.

Reaction of Dimethylberyllium with Ethylenediamines.—*Tetramethylethylenediamine.* The diamine (1·4 g., 0·012 mole) in ether (2 c.c.) was added to dimethylberyllium (10 c.c., 1M-solution in ether) contained in one limb of a double Schlenk tube.[12] Reaction was noticeably exothermic. Ether was distilled from the solution until *dimethyl*-(NNN′N′-*tetramethylethylenediamine*)-*beryllium*(I) crystallized. The product was separated by filtration on the sintered disc connecting the two limbs of the double Schlenk tube, and solvent and excess of amine were removed by pumping; the product had m. p. 81—82° (Found: Be, 5·5; CH_3, by hydrolysis, 19·6%; *M*, cryoscopically in 0·29, 0·64 wt. % benzene, 176, 170. $C_8H_{22}BeN_2$ requires Be, 5·8; hydrolyzable CH_3, 19·3%; *M*, 155). The complex fumes strongly in air, but does not inflame; it reacts vigorously with water with effervescence.

NNN′-*Trimethylethylenediamine.* Dimethylberyllium (0·00232 mole in 0·8 c.c. of ether) was cooled, by liquid air, in a bulb attached to the vacuum-line, and the diamine (0·255 g., 0·00250 mole) condensed on it. The mixture was allowed to warm to room temperature, and at 18° vigorous effervescence occurred with deposition of colourless needles. The gas (49·6N-c.c., 0·00222 mole) was identified as methane by its infrared spectrum. The *product* (III) was then hydrolyzed by water vapour, and methane (56·7N-c.c., 0·00253 mole) collected.

In another reaction dimethylberyllium (0·00264 mole) was mixed with the diamine (1·23 g., 0·012 mole) in excess. After effervescence at room temperature had ceased, the mixture was heated at 60° for $\frac{1}{2}$ hr., but scarcely any further gas evolution was observed [Found: CH_4, 57·4N-c.c. $(C_6H_{16}BeN_2)_n$ requires CH_4, 59·0N-c.c., 0·00264 mole].

In a larger-scale preparation (0·0058 mole of dimethylberyllium) carried out in a double Schlenk tube, the product was separated by cooling its ether solution, filtration, and pumping free from solvent and slight excess of diamine; it formed colourless needles, m. p. 116—118° (Found: CH_3, by hydrolysis, 11·3%; *M*, cryoscopically in 0·77, 1·16 wt. % benzene, 255, 241. $C_{12}H_{32}Be_2N_4$ requires hydrolyzable CH_3, 12·0%; *M*, 250).

NN′-*Dimethylethylenediamine.* The diamine (0·354 g., 0·004 mole) was condensed on dimethylberyllium (0·00218 mole in 0·75 c.c. of ether) cooled in liquid air. Methane (48·2N-c.c., 0·00215 mole) was evolved and collected from the reaction mixture. When ether and the excess of diamine were removed by pumping, the *complex* crystallized as colourless needles (IV) (Found: *M*, cryoscopically in 0·81, 1·41 wt. % benzene, 222, 217. $C_{10}H_{28}Be_2N_4$ requires *M*, 222).

The dimer (IV) (0·00109 mole), heated in a vacuum, gave methane (39·1N-c.c., amounting to 80% of the remaining methyl bound to beryllium).

A further quantity of dimer (IV) (0·0145 mole) was prepared in ether solution. The ether was removed by distillation, tetralin (120 c.c.; free from peroxides and distilled from sodium at 206—208°) was added, and the resulting solution heated at 140—150° until gas evolution ceased (2 hr.). The resulting pale yellow gel was allowed to cool to 80—100° and tetralin removed by distillation under reduced pressure, giving a cream-coloured solid which was washed with dry ether (30 c.c.) and dried in a vacuum. Hydrolysis of part of the product with 2N-sulphuric acid yielded no methane, but liberated some tetralin which had evidently been trapped in the polymer [Found: Be, 8·1; $C_2H_4(NHMe)_2$, 78·2%; ratio Be : N, 1 : 1·97]. The product therefore contained 15% of tetralin, some of which could be removed by prolonged pumping at 150—200° in a vacuum.

NN-*Dimethylethylenediamine.* The diamine (0·59 g., 0·0067 mole) was condensed on dimethylberyllium (0·00290 mole) in a little ether. When the diamine melted a colourless crystalline solid appeared (this must have been the complex [Me_2Be diamine]) and redissolved as the temperature increased. A vigorous exothermic reaction began just below room temperature, with evolution of methane (64N-c.c., 0·00286 mole) and deposition of colourless needles of a *dimer* (Found: *M*, cryoscopically in 0·47, 0·70 wt. % benzene, 222, 224. $C_{10}H_{23}Be_2N_4$ requires *M*, 222).

The behaviour of the dimer when heated has already been described (after $1\frac{1}{2}$ hr. at 170°, 0·2810 g. of dimer yielded CH_4, 54·2N-c.c. $C_{10}H_{28}Be_2N_4$ requires CH_4, 56·6N-c.c.).

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[12] Fischer, Hafner, and Stahl, *Z. anorg. Chem.*, 1955, **282**, 47.

Ethylenediamine. An excess of diamine (0·537 g.) was condensed on dimethylberyllium (0·00241 mole) in a little ether. Vigorous evolution of methane began at about −20° and after an hour at room temperature 90·6N-c.c. were collected. After a further ½ hr. at 45° an additional 10·9N-c.c. of methane were collected, giving a total of 101·5N-c.c. (0·00453 mole); the formation of $(C_2H_4N_2H_2Be)_x$ would require 108N-c.c. Addition of water to the product yielded the rest of the beryllium-methyl (7·5N-c.c. of methane).

(1,2-*Dimethoxyethane*)*dimethylberyllium*, $[Me_2(MeO{\cdot}C_2H_4{\cdot}OMe)Be]$.—Prepared from 1,2-dimethoxyethane and dimethylberyllium in ether solution, this was precipitated as colourless feathery needles which were separated, pumped dry, and recrystallized from ether. The *complex*, m. p. 100—101°, sublimes at 60—70°/0·06 mm. and condenses as colourless prisms (Found: CH_3, by hydrolysis, 23·1%; *M*, cryoscopically in 0·37, 0·73 wt. % benzene, 123, 125. $C_6H_{16}BeO_2$ requires hydrolyzable CH_3, 23·2%; *M*, 129). The complex soon inflames when exposed to the air (not immediately, like dimethylberyllium).

Bipyridyl Complexes.—Bipyridyldimethylberyllium, $[Me_2\ bipy\ Be]$.—Bipyridyl (3·8 g.) in ether (150 c.c.) was added to an equimolar quantity of dimethylberyllium in ether (~10 c.c.). The bright yellow precipitate formed immediately was separated and washed with ether, in which it is only sparingly soluble. The *product* was purified by extraction (Soxhlet) with benzene, in which it gave a deep orange solution which gradually deposited golden-yellow needles, decomp. from 170° (Found: Be, 4·60, 4·46; CH_3, by hydrolysis, 14·8. $C_{12}H_{14}BeN_2$ requires Be, 4·61; hydrolyzable CH_3, 15·4%). Hydrolysis with aqueous sodium hydroxide followed by extraction with light petroleum yielded 96% of the theoretical amount of bipyridyl. The complex appears unaffected by dry air, in contrast to dimethylberyllium which immediately inflames. It becomes white after about 15 minutes' exposure to normal air. It sublimes very slowly at 135—140°/0·003 mm.

Bipyridyldiethylberyllium, $[Et_2\ bipy\ Be]$. This was prepared similarly, and precipitated more slowly as red needles, which were washed with a little ether and dried in a vacuum; it decomposed from 90° (Found: Be, 4·25, 3·98; C_2H_5, by hydrolysis, 25·5%; *M*, cryoscopically in 0·78, 0·91 wt. % benzene, 233, 220. $C_{14}H_{18}BeN_2$ requires Be, 4·04; hydrolyzable C_2H_5, 26·0%; *M*, 223). The *diethyl complex* is only moderately soluble in diethyl ether, and is more soluble in benzene. In the air it becomes white in about 10 min., does not appear affected by dry air, and may be sublimed very slowly with slight decomposition at 100°/0·0015 mm. It does not react with benzophenone in boiling ether.

Bipyridyldiphenylberyllium, $[Ph_2\ bipy\ Be]$. This was immediately precipitated when bipyridyl (2·93 g., 0·0187 mole) in ether (50 c.c.) was added to diphenylberyllium (0·0187 mole, from phenyl-lithium and beryllium chloride) in ether (100 c.c.). It is only sparingly soluble in ether and in benzene, and crystallized as pale yellow needles on extraction (Soxhlet) with benzene (Found: Be, 2·78, 2·79; bipyridyl, 48·45. $C_{22}H_{18}BeN_2$ requires Be, 2·82; bipyridyl, 48·9%). The *diphenyl complex* is hydrolyzed very slowly in contact with cold water, but is readily decomposed by warm dilute sulphuric acid.

The halide complexes were all precipitated by addition of bipyridyl to an ether solution of the appropriate halide (beryllium iodide having been prepared by reaction of iodine with diethylberyllium in ether). *Dichloro*(*bipyridyl*)*beryllium* formed colourless needles from nitrobenzene; it decomposed very slowly above 330° and did not melt when heated to 360° (Found: Be, 3·51, 3·64; Cl, 30·0. $C_{10}H_8BeCl_2N_2$ requires Be, 3·81; Cl, 30·1%). *Dibromo*(*bipyridyl*)-*beryllium* (Found: Br, 48·9. $C_{10}H_8BeBr_2N_2$ requires Br, 49·2%) and *di-iodo*(*bipyridyl*)*beryllium* (Found: I, 60·3. $C_{10}H_8BeI_2N_2$ requires I, 60·6%), like the dichloro-compound, are very sparingly soluble in ether, but a little more soluble in tetrahydrofuran.

Bipyridyldimethylzinc, $[Me_2\ bipy\ Zn]$. Dimethylzinc (0·0360 mole) was condensed on bipyridyl (0·0100 mole) in a flask connected to a vacuum-line. As the dimethylzinc melted a bright yellow colour developed. After ½ hr. at room temperature the excess of dimethylzinc (0·0255 mole) was recovered by pumping, and was measured as gas. Therefore 0·0105 mole of dimethylzinc had reacted with 0·0100 mole of bipyridyl. The complex slowly darkens from 100°; it is only sparingly soluble in diethyl ether.

Bipyridyldiethylzinc, $[Et_2\ bipy\ Zn]$. Bipyridyl (1·2 g., 0·0077 mole) in ether (10 c.c.) was added to diethylzinc (1·0 g., 0·0081 mole) in ether (15 c.c.) contained in one limb of a double Schlenk tube. Evaporation of solvent from the resulting red solution yielded the *complex* as orange-red plates (Found: C_2H_5, by hydrolysis, 20·5. $C_{14}H_{18}N_2Zn$ requires hydrolyzable C_2H_5, 20·8%).

Bipyridyldimethylcadmium, [Me_2 bipy Cd]. When dimethylcadmium (excess) and diethyl ether were condensed on bipyridyl, a bright yellow compound was formed which (unlike bipyridyl) was only sparingly soluble in ether. Removal of ether and the excess of dimethylcadmium by pumping at room temperature resulted in a gradual fading of the colour, until only colourless bipyridyl remained.

Dimethyl-(o*-phenanthroline*)*zinc*, [Me_2 *o*-phenan Zn].—Anhydrous (sublimed) *o*-phenanthroline (0·00305 mole) absorbed dimethylzinc vapour (0·00350 mole) at room temperature with formation of a yellow complex, slightly paler than the bipyridyl compound. It becomes white in the air in about an hour, and slowly effervesces in water.

Pyridine Complexes.—Dimethyldipyridineberyllium, [Me_2 py_2 Be]. Dry pyridine (1·9 g., 0·024 mole) in ether (2 c.c.) was added to dimethylberyllium (0·010 mole) in ether (10 c.c.) contained in one limb of a double Schlenk tube. The very pale yellow solution resulting from the perceptibly exothermic reaction was filtered into the other limb, and gradually deposited colourless needles, m. p. 91—92° to a yellow liquid (Found: CH_3, by hydrolysis, 15·2. $C_{12}H_{16}BeN_2$ requires hydrolyzable CH_3, 15·2%). The *complex* fumes strongly in the air and is very rapidly decomposed by water.

Diethyldipyridineberyllium, [Et_2 py_2 Be]. This was similarly prepared, but is more soluble in ether. The *complex* separated as orange-yellow needles when the yellow solution had been concentrated by evaporation (Found: C_2H_5, by hydrolysis, 25·1%; *M*, cryoscopically in benzene, 214. $C_{14}H_{20}BeN_2$ requires hydrolyzable C_2H_5, 25·8%; *M*, 225). It darkens gradually from 90° to 100°, and decomposes rapidly above 140° without melting.

Bipyridyl Anion Complexes.—Bisbipyridylberyllium, [$bipy_2$ Be]. Lithium in excess (*ca.* 1 g.) was added to bipyridyl (1·2 g.) in 1,2-dimethoxyethane (50 c.c.). The solution quickly became purple-red and then gradually deep green; it was set aside for 24 hr. to ensure complete formation of the dilithium adduct and then added to a suspension of [Cl_2 bipy Be] obtained by the addition of bipyridyl (1·28 g.) in ether (10 c.c.) to anhydrous beryllium chloride (0·65 g.) in 1,2-dimethoxyethane (50 c.c.) contained in a double Schlenk tube. The [Cl_2 bipy Be] quickly dissolved, giving a deep green solution, which was evaporated to dryness by pumping at room temperature. The black residue was extracted with dry benzene (40 c.c.), and the extract twice filtered through sintered-glass discs (porosity 3) to separate lithium chloride and any excess of [Cl_2 bipy Be]. Benzene was then pumped from the dark olive-green filtrate, the residue finally being heated to 35° for 2 hr. in a vacuum. The black product was broken to a finely crystalline glistening powder, and washed with ether (2 × 10 c.c.) to remove any trace of free bipyridyl. The *complex* has not been observed to melt but it sublimes very slowly at $180°/\sim10^{-4}$ mm., with a little decomposition since a small amount of bipyridyl was deposited on the cooler parts of the condenser (Found: Be, 2·9; bipyridyl, colorimetrically, 95·1. $C_{20}H_{16}BeN_2$ requires Be, 2·8; bipyridyl, 97·2%). Halogen could not be detected in the product.

The complex is sparingly soluble in diethyl ether, more readily so in tetrahydrofuran or in 1,2-dimethoxyethane; in these solvents the colour is deep green. It is also moderately soluble in benzene, but the solution is then of a brownish-olive-green colour.

Addition of bromine (1 mol.) in ether to a solution of the complex in diethyl ether immediately discharged the green colour, and the pale cream [Br_2 bipy Be] was precipitated.

Lithium bisbipyridylberyllate, Li[$bipy_2$ Be]. Dichloro(bipyridyl)beryllium (0·0075 mole) was precipitated by adding bipyridyl (2·34 g., 0·015 mole) in ether (50 c.c.) to beryllium chloride (0·60 g., 0·0075 mole) in ether (50 c.c.). After the addition of lithium (0·25 g.) the mixture was stirred. A green colour, due to [$bipy_2$ Be], soon developed and after an hour all the suspended [Cl_2 bipy Be] had dissolved. With continued stirring the colour changed through brown to deep violet-blue. The solution was filtered from lithium chloride and excess of lithium and was introduced into a double Schlenk tube, and solvent was removed by pumping. The residue was extracted with dry benzene, in which it dissolved with a brown-violet colour, and filtered into the other limb of the double Schlenk tube. Removal of benzene by pumping yielded the *lithium salt* as a black microcrystalline glistening powder (Found: Li, 2·24; Be, 2·58. $C_{20}H_{16}BeLiN_2$ requires Li, 2·14; Be, 2·74%).

Addition of bromine in ether to a solution of the lithium salt in the same solvent resulted in a colour change from violet to green, followed by precipitation of pale cream [Br_2 bipy Be].

Beryllium Chloride Complexes.—Dichloro-(1,2-*dimethoxyethane*)*beryllium*, [$Cl_2(MeO{\cdot}CH_2{\cdot}CH_2{\cdot}OMe)Be$]. This was obtained as a fine precipitate when 1,2-dimethoxyethane in diethyl ether was added to beryllium chloride in the same solvent. The *complex*, when washed with ether and dried by pumping, had m. p. 237—244° (decomp.) (Found: Cl, 41·5. $C_4H_{10}BeCl_2O_2$ requires Cl, 41·8%). The very hygroscopic complex is only sparingly soluble in diethyl ether, insoluble in benzene and other non-polar solvents, and is decomposed by ethanol. This complex has previously been described[11] as $Cl_2Be(MeO{\cdot}C_2H_4{\cdot}OMe)_2$, although the analysis given corresponds to $Cl_2Be(MeO{\cdot}C_2H_4{\cdot}OMe)$.

Dichlorobis(dimethyl sulphide)beryllium, $[Cl_2(Me_2S)_2Be]$. This crystallized when a solution of anhydrous beryllium chloride in dimethyl sulphide was cooled; it had m. p. 117—119° (Found: Cl, 35·1%; *M*, cryoscopically in 0·53, 0·88 wt. % benzene, 217, 209. $C_4H_{12}BeCl_2S_2$ requires Cl, 34·8%; *M*, 204). The *bis-sulphide complex* fumes slightly in air, and liquefies rapidly; it reacts vigorously with water, dissolves exothermally in diethyl ether, and is soluble in dimethyl sulphide, benzene, and toluene. When it was dissolved in toluene and solvent was then removed by pumping at room temperature *di-μ-chloro-dichlorobis(dimethyl sulphide)diberyllium*, $[Cl(Me_2S)BeCl_2Be(Me_2S)Cl]$, crystallized as colourless prisms, m. p. 135° (decomp.) (Found: Cl, 50·2%; *M*, cryoscopically in benzene, 278. $C_4H_{12}Be_2Cl_4S_2$ requires Cl, 50·0%; *M*, 284). This complex also liquefies rapidly in air, and the dimethyl sulphide is evidently displaced by diethyl ether in which the complex dissolves exothermically.

Dichloro-1,2-*dimethylthioethaneberyllium*, $[Cl_2(MeS{\cdot}CH_2{\cdot}CH_2{\cdot}SMe)Be]$, was formed as fine colourless feathery needles when anhydrous beryllium chloride was stirred with a benzene solution of the dithioether. The very deliquescent product was washed with pentane (Found: Cl, 34·4. $C_4H_{10}BeCl_2S_2$ requires Cl, 35·1%). The complex fumes in the air, and is only sparingly soluble in benzene.

Beryllium chloride dissolves readily in diethyl sulphide, but hydrogen chloride is slowly formed. A concentrated solution increases in viscosity and gradually sets to an orange solid.

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