Beryllium–Nitrogen π-Bonding: the *X*-Ray Structure of Bis(di-t-butylmethyleneamino)beryllium dimer, $[Be(N{:}CBu^t_2)_2]_2$

By JOHN B. FARMER, HARRISON M. M. SHEARER, J. DAVID SOWERBY, and KENNETH WADE*
(*Chemistry Department, Durham University Science Laboratories, South Road, Durham* DH1 3LE)

Summary *X*-Ray crystal structure analysis of bis(di-t-butylmethyleneamino)beryllium dimer, $[Be(N{:}CBu^t_2)_2]_2$, prepared from the ketimine $Bu^t_2C{:}NH$ and di-isopropylberyllium, shows that it adopts a structure containing both bridging and terminal methyleneamino-groups, the latter attached to the 3-co-ordinate metal atoms by Be–N bonds only 150 pm long, the shortest yet reported for a solid beryllium–nitrogen compound.

COMPOUNDS containing beryllium–nitrogen multiple bonds have attracted much interest recently.[1] Structural studies on the amino-derivatives $[Be(NMe_2)_2]_3$,[2] $MBe(NH_2)_3$ (M = K or Rb),[3] and $Be[N(SiMe_3)_2]_2$[4] have shown their amino-groups to be attached to their co-ordinatively unsaturated beryllium atoms by short Be–N bonds (157, 159, and 156 pm respectively), indicative of N ⇌ Be dative π-bonding. We here report the first structural study of a methyleneamino-derivative of beryllium, $[Be(N{:}CBu^t_2)_2]_2$, (I), which con-

tains both bridging and terminal methyleneamino groups, the latter attached to the 3-co-ordinate metal atoms by the shortest Be-N bonds yet found.

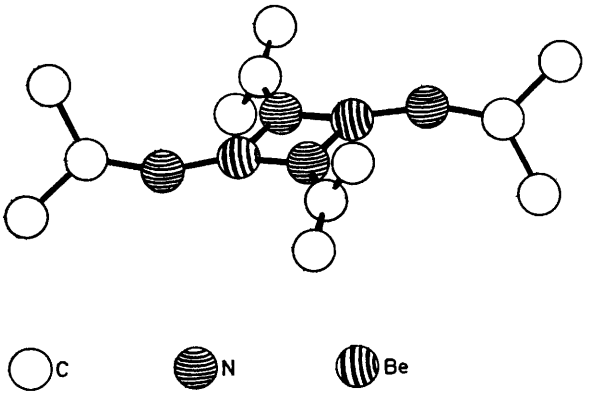

FIGURE. Skeleton of $[Be(N:CBu^t_2)_2]_2$. Interatomic distances (pm): Be–N_μ 168; Be–N_t 150; C=N_μ 128; C=N_t 127; Be · · · Be 223. Bond angles (°): Be–N_μ–Be′ 83; N_μ–Be–N_μ′ 97; Be′ · · · Be–N_t 161; Be–N_t=C 161; N_t–Be–N_μ 129; Be–N_μ=C 138.

Compound (I) is readily prepared from $BePr^i_2$ and $2Bu^t_2C:NH$ in diethyl ether, and crystallises from hexane as pale yellow needles, m.p. 220—230 °C (decomp.), analysing satisfactorily for $C_{36}H_{72}Be_2N_4$. The crystals are monoclinic, with $a = 1776{\cdot}5$, $b = 1526{\cdot}1$, and $c = 1691{\cdot}5$ pm, $\beta = 118{\cdot}52°$, space group $C2/c$, $Z = 4$. The intensity data were collected on a Hilger and Watts four-circle diffractometer, using Zr-filtered Mo radiation, to a limit of $\theta = 22{\cdot}5°$. The structure was solved by means of the Patterson function and refined by full-matrix least-squares methods to $R = 0{\cdot}127$ for the 1351 reflections with net counts $\geqslant 2\sigma$.

The molecules of $[Be(N:CBu^t_2)_2]_2$ are centro-symmetric (see Figure). The metal atoms are linked by bridging methyleneamino-units lying not, as expected, in the plane of the $(BeN)_2$ ring, but twisted about the C=N · · · N=C axis by 37°. Each metal atom also has one terminal methyleneamino ligand attached by *non*linear C=N–Be units; the terminal ligands are bent progressively away from the $(BeN)_2$ plane in two stages, the angles Be′ · · · Be–N_t and Be–N_t=C being 161°. These distortions from the expected structure can be ascribed to repulsions between the bulky t-butyl substituents, which prevent the skeletons of the bridging methyleneamino-units from lying in the $(BeN)_2$ plane, and also prevent the linear C=N⇌Be arrangements which would allow maximum dative π-bonding between the terminal methyleneamino-nitrogen atoms and the metal atoms. However, this slight departure from linearity does not lead to significant loss of multiple bond character in the terminal N ⇌ Be bonds, which are only 150 pm in length (*cf.* the bridging Be–N bonds, 168 pm long. Other interatomic distances and bond angles are given beneath the Figure). Compound (I) thus adopts the type of structure deduced for compounds $[Be(N:CR^1R^2)_2]_2$ from their i.r. spectra, in which 'high' frequency (*ca.* 1730 cm^{-1}) azomethine stretching absorptions, ν(C=N), were taken to be indicative of the presence of linear C=N⇌Be units.[5] This interpretation is essentially substantiated by the present work; (I) absorbs at 1721 cm^{-1} [$\nu(C{=}N)_t$] and 1631 cm^{-1} [$\nu(C{=}N)_\mu$]. The ^1H n.m.r. spectrum of (I) (toluene solution) contains an incompletely resolved doublet (τ 8·69, 8·71) attributable to the terminal ligands, and a singlet (τ 8·77) attributable to the bridging ligands, of appropriate relative intensities (1 : 1 : 2).

The magnesium and zinc analogues of (I) have similar spectra, *e.g.* $[Mg(N:CBu^t_2)_2]_2$ (from $MgEt_2 + 2Bu^t_2C:NH$) has ν(C=N) 1664 and 1605 cm^{-1}, while $[Zn(N:CBu^t_2)_2]_2$ (from $ZnMe_2 + 2Bu^t_2C:NH$, or from $ZnCl_2 + 2Bu^t_2C:NLi$) has ν(C=N) 1683 and 1585 cm^{-1}, and are believed to adopt similar structures.

Compound (I) thus establishes for a Group II metal the use of methyleneamino groups $R_2C:N$ as probes for the study of N ⇌ M dative π-bonding, hitherto applied to Group III [$(mesityl)_2BN:CPh_2$[6] and $LiAl(N:CBu^t_2)_4$[7]] and Group IV [$M(N:CPh_2)_4$ (M = Si, Ge or Sn)[10]] examples.

We thank the S.R.C. for grants (to J.B.F. and J.D.S.)

(*Received*, 19*th January* 1976; *Com.* 048.)

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