Bis(1,4-di-*tert*-butyl-1,4-diazabutadiene)gallium is not a Gallium(II) Compound

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The recently reported paramagnetic compounds $(dbdab)_2M$ (dbdab = 1,4-di-*tert*-butyl-1,4-diazabutadiene, M = Ga, Al), both contain trivalent metal bound to one singly and one doubly reduced dbdab ligand; the larger metal hyperfine coupling in the EPR spectrum of the gallium complex is not due to a gallium(II) oxidation state, it is simply a result of the quite large isotropic hyperfine coupling constants of [69]Ga and [71]Ga as demonstrated previously for the related radicals $(bpy^{-·})M^{III}Me_2$ (bpy = 2,2'-bipyridine).

Three recent communications in this journal by Cloke, Raston and coworkers[1-3] have referred to the title compound **1** as a unique example of a monomeric gallium(II) complex.[1] This assignment was based on the dominance of the EPR spectrum[3] by a quartet of about 18 G[1] due to gallium isotopes [69]Ga and [71]Ga (Table 1), whereas a structurally very similar aluminium analogue **2** did not exhibit a similarly metal isotope([27]Al)-dominated EPR signal.[3] Neither of the EPR hyperfine structures was adequately analysed. A questionable simulation of the poorly resolved spectrum of **1** was offered in ref. 1, whereas a spectrum with several equidistant lines (spacing *ca.* 5 G) was presented for **2** in ref. 3.

The absence of a central line in the EPR spectrum of **2** proves the presence of an uneven number of nuclei with non-integer nuclear spin: [27]Al ($I = 5/2$). An EPR computer simulation of **2** involving [27]Al coupling was only possible assuming 1 Al, 2 N and 2 H nuclei with virtually identical coupling of about 5 G (Fig. 1), suggesting a localized
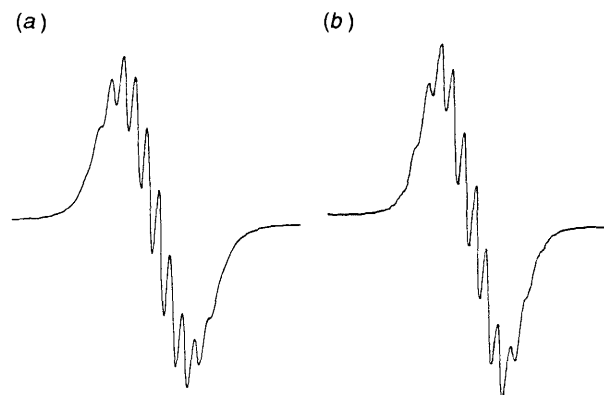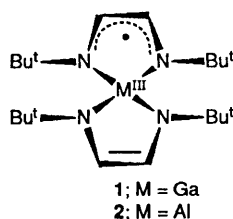

Fig. 1 Computer simulation (*a*) of the reported EPR spectrum[3] of $(dbdab)_2Al$; (*b*) 1 [27]Al, 2 [14]N (1,4) and 2 [1]H (2,3) nuclei with 5 G hyperfine coupling; line width 5 G (Lorentzian line shape).

1; M = Ga
2; M = Al

Table 1 EPR coupling constants

Coupling constant in G[a]	Isotopes (nat. abundance)		
	^{27}Al (100%)[b]	^{69}Ga (60.2%)[c]	^{71}Ga (39.8%)[c]
A_{iso} (ref. 9)	983	2667	3389
a_M: (bpy$^{-\bullet}$)MMe$_2$ (ref. 4)	4.04	11.85	15.05
a_M: (dbdab$^{-\bullet}$)M(dbdab^{2-})	≈5	≈18 (average)	

[a] $1 G = 10^{-4}$ T. [b] $I = 5/2$. [c] $I = 3/2$.

description (dbdab$^{-\bullet}$)Al^{III} (dbdab^{2-}) as supported by a correct interpretation of crystallography. The magnitude of 5 G for all three coupling constants is in agreement with previous data for Al^{III} radical chelate complexes[4] and dbdab$^{-\bullet}$ complexes.[5-7] Similarly, the poorly resolved ligand hyperfine splitting[1] of the Ga complex **1** does not support a delocalized system which would have to exhibit half the coupling constant of approximately 5 G for four 1,4-nitrogen atoms and four 2,3-hydrogen nuclei.[8]

The isotropic hyperfine coupling constants A_{iso}[9] and the experimental metal hyperfine splitting for the related radical complexes (bpy$^{-\bullet}$)MMe$_2$[4] (bpy = 2,2′-bipyridine) in Table 1 show that the metal coupling of gallium(III) radical complexes should be larger by a factor of about 2.8 (^{69}Ga) or 3.6 (^{71}Ga) than that for ^{27}Al in a corresponding aluminium complex, assuming comparable spin transfer. Starting from a coupling of 5 G in the (dbdab)$_2$Al^{III} complex, a number of 18 G for an (average) gallium coupling would be just expected for a Ga^{III} analogue. Secondly, the somewhat higher metal coupling in what really are (dbdab$^{-\bullet}$) complexes as compared to (bpy$^{-\bullet}$) complexes is a typical consequence of the higher spin density at nitrogen in the smaller diimine anion radical.[5] Thirdly, the

relation $a_{exp}/A_{iso} = 0.0067$ for the gallium example indicates a very small participation of the metal at the singly occupied MO as is characteristic for anion radical complexes of diamagnetic metal centres.[4,6]

Finally, Cloke *et al.*[3] correctly state that the distances within the two rather different dbdab ligands are, within three standard deviations, very similar in the Al and Ga complex. However, the ligand with the C(2)–C(3) bond length of about 139 pm[1,3] was not correctly identified as an anion radical ligand (bond order 1.5). A neutral ligand was suggested which, however, should have a much longer C(2)–C(3) single bond distance of 148 pm as obtained for the related (dbdab)ZnMe$_2$[7] and similar complexes.[10] In view of the radius problem for the elements of main group 3, the differences in the metal–nitrogen bond lengths are not suitable as a basis for the assignment of unique oxidation states. In conclusion, both complexes **1** and **2** are clearly metal(III) complexes (dbdab^{2-})M^{III} (dbdab$^{-\bullet}$) with localized mixed-valent α-diimine ligands[8] in the crystal and on the EPR time scale in solution.

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References

1 F. G. N. Cloke, G. R. Hanson, M. J. Henderson, P. B. Hitchcock and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1989, 1002.
2 M. J. Henderson, C. H. L. Kennard, C. L. Raston and G. Smith, *J. Chem. Soc., Chem. Commun.*, 1990, 1203.
3 F. G. N. Cloke, C. I. Dalby, M. J. Henderson, P. B. Hitchcock, C. H. L. Kennard, R. N. Lamb and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1990, 1394.
4 W. Kaim, *Chem. Ber.*, 1981, **114**, 3789; W. Kaim, *Z. Naturforsch., Teil B*, 1982, **37**, 783.
5 H. Tom Dieck, K. D. Franz and F. Hohmann, *Chem. Ber.*, 1975, **108**, 163.
6 W. Kaim, *Coord. Chem. Rev.*, 1987, **76**, 187.
7 M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. van Koten, E. Wissing, W. J. J. Smeets and A. L. Spek, *J. Am. Chem. Soc.*, in the press.
8 Cf. W. Kaim, S. Ernst and V. Kasack, *J. Am. Chem. Soc.*, 1990, **112**, 173.
9 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.
10 G. van Koten and K. Vrieze, *Adv. Organometal. Chem.*, 1982, **21**, 153.