

validity of this treatment of powder data owing to the strong correlation between D and $z'J'$. In this complex the close fit of the data to eqn. (1) indicates that intra-dimer exchange dominates. Strong antiferromagnetic coupling in $[\{(HL^1)Ni(NCS)\}_2(CO_3)]^{2+}$ may be rationalised on the basis of a superexchange pathway in which the $Ni^{II} d_{z^2}$ (magnetic) orbitals interact *via* the μ -carbonato O-bridge. This linear Ni–O–Ni linkage provides ideal geometry for the exchange, which in dicopper(II) complexes is known to result in diamagnetism.^{6a} A complex formulated as a μ -hydroxo-bridged dinickel(II) dimer, $[\{(tren)NiOH\}_2OH]^+$ [tren = tris-(2-aminoethyl)amine], is also reported to be diamagnetic, presumably owing to superexchange.¹¹

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The First Lithium Phenolate with a Trinuclear Structure and the Tetranuclear Product of 1 : 1 Addition of Lithium Iodide; X-Ray Structures of $[LiOAr]_3$ and $[Li_2(OAr)I]_2$ [OAr = $OC_6H_2(CH_2NMe_2)_2-2,6-Me-4$]

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Reaction of 2,6-bis[(dimethylamino)methyl]-4-methylphenol with *n*-butyllithium affords quantitatively $[LiOAr]_3$ [OAr = $OC_6H_2(CH_2NMe_2)_2-2,6-Me-4$] **1**, which has an unprecedented trinuclear structure both in solution (cryoscopy in C_6H_6) and in the solid state (X-ray); **1** reacts selectively with LiI to form the adduct $[Li_2(OAr)I]_2$ **2** which has a tetranuclear structure (X-ray).

Phenolate and alcoholate groups can be used as spectator ligands in organometallic chemistry in much the same way as phosphines or cyclopentadienyls, and their bulk can be selected to favour specific coordination numbers and geometries.¹ Our work involves the use of aryl ligands with tertiary amine substituents, which through intramolecular coordination can stabilize reaction intermediates or change the reactivity of a metal centre by blocking specific coordination sites.² In a related extension of this work we are now using the interesting properties of bulky phenolate ligands containing potentially coordinating substituents to develop a new, broad field of inorganic as well as organometallic chemistry. With the X-ray structure of the copper phenolate $[Cu_2(\mu-Br)\{\mu-OC_6H_3(CH_2NMe_2)_2-2,6\}\{P(OMe)_3\}_2]$ we have already demonstrated the interesting potential of a phenolate ligand with two *ortho*-chelating tertiary amine substituents.³ Recently the structure of a tetranuclear barium complex, containing a related phenolate ligand, was published.⁴ We now report the syntheses and structural aspects of both a lithium phenolate with an unprecedented trinuclear structure

in solution and in the solid state, and its tetranuclear 1 : 1 lithium iodide adduct.

The reaction of *n*-butyllithium with 2,6-bis[(dimethylamino)methyl]-4-methylphenol in hexane at 0 °C in a 1 : 1 molar ratio affords the lithium phenolate **1** quantitatively. Complex **1** was obtained as colourless crystals by cooling a saturated hexane solution to –30 °C. It is a moisture-sensitive solid which can be handled in air for short periods but which must be stored under an inert atmosphere for longer periods.

Elemental analysis and ¹H NMR data of **1**[†] are consistent with the formulation $[LiOC_6H_2(CH_2NMe_2)_2-2,6-Me-4]_n$.

[†] Analytical data for **1**: ¹H NMR (C_6D_6 , 300 MHz, 298 K): δ 6.93 (s, 2H, *meta*-H); 3.32 (br s, 4H, CH_2N); 2.34 (s, 3H, *para*-Me); 1.92 (s, 12H, NMe_2). Calc. for $C_{39}H_{63}Li_3N_5O_3$: C, 68.4; H, 9.3; N, 12.3. Found: C, 68.3; H, 9.1; N, 12.15%. Relative molecular mass determination by cryoscopy (0.50 g in 24.22 and 52.56 g of benzene): Calc. for monomer: 228.3 Found: 660 and 672 (degree of association: 2.9).

Cryoscopy measurements on **1** showed it to be a trimer in benzene in the concentration range of 0.037–0.080 mol dm⁻³. To determine the stereochemistry of **1**, and its degree of association in the solid state, an X-ray structure determination was carried out.‡

The crystal structure consists of the packing of four discrete trimeric molecules in the unit cell, and each trimeric unit possesses a pseudo-threefold rotation axis. Two views of the molecular geometry of **1** are shown in Fig. 1.

Complex **1** is the first isolated and characterized lithium phenolate with a trinuclear structure. Since **1** in solution also appears to have a trimeric structure this molecular arrangement must be particularly stable and the origins of this stability are reflected in various geometric parameters. Firstly, the Li–O bond lengths [average 1.865(9) Å] are comparable with the shortest ever reported in related complexes, e.g. dimeric lithium 2,6-di-*tert*-butyl-4-methylphenolate, **3**.⁵ Secondly, the C_{ipso}–O distances are very short and range from 1.301(6) to 1.326(6) Å, while corresponding distances in **3** as well as in lithium enolates derived from ketones are close to 1.35 Å.⁶ In **1** there is an almost perfectly planar Li₃O₃ six-membered ring, see view (b) in Fig. 1 (maximum least-squares deviation is 0.05 Å). In this ring the Li–O–Li and O–Li–O angles are in the ranges 126.5–129.7 and 110.1–112.4°, respectively, and Σ = 720.0°.

The short Li–O and C_{ipso}–O bond lengths can be explained in terms of quasi-aromaticity of the Li₃O₃ ring;⁷ the delocalized π-electrons, originating from the lone pairs of the oxygen atoms, slightly change the hybridization of the oxygen atoms from sp³ to more sp² with a concomitant shortening of the bond lengths to oxygen.

Adjacent lithium atoms are N-coordinated by different CH₂NMe₂ substituents of their mutually O-bridging phenolate ligand, and the orientation of these ligands with respect to the Li₃O₃ ring provides a 'propeller-like' molecule with each trimer having screw-type chirality. (Both enantiomers are present in the crystal structure.) In these molecules each of the six equivalent CH₂NMe₂ substituents has inequivalent CH₂

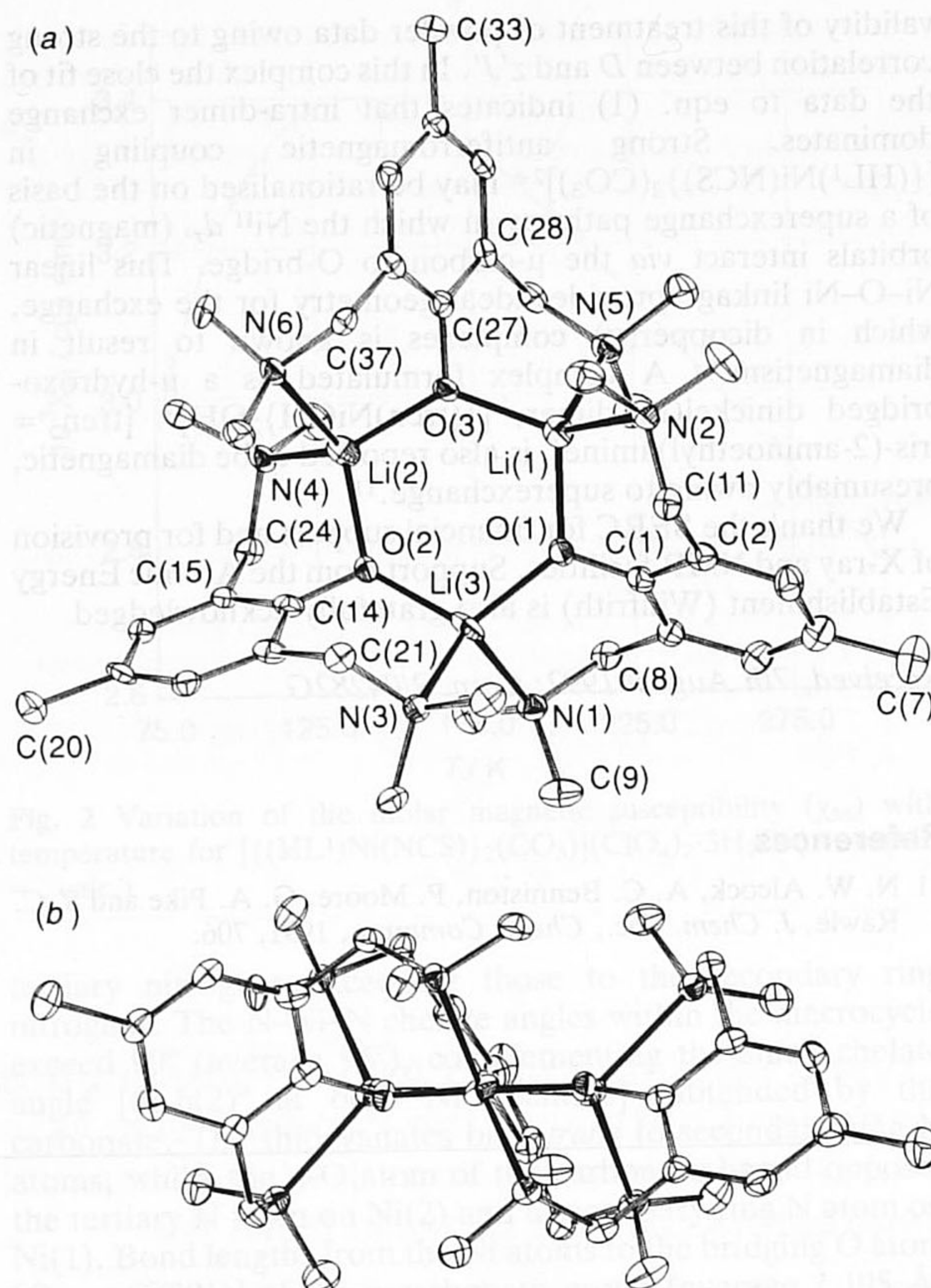


Fig. 1 Molecular structure of [LiOC₆H₂(CH₂NMe₂)₂-2,6-Me-4]₃, **1**; ORTEP drawings with 50% probability ellipsoids viewed (a) perpendicular to and (b) along the Li₃O₃ plane. Selected bond lengths (Å) and angles (°): Li(1)–O(1), 1.878(9); Li(1)–O(3), 1.869(9); Li(2)–O(3), 1.846(9); Li(2)–O(2), 1.887(9); Li(3)–O(2), 1.828(9); Li(3)–O(1), 1.881(9); Li(1)–N(2), 2.256(9); Li(1)–N(5), 2.223(9); Li(2)–N(4), 2.233(9); Li(2)–N(6), 2.325(9); Li(3)–N(1), 2.163(9); Li(3)–N(3), 2.227(9); O(1)–C(1), 1.301(6); O(2)–C(14), 1.326(6); O(3)–C(27), 1.324(6); O(1)–Li(1)–O(3), 112.0(4); Li(1)–O(1)–Li(3), 126.5(4); O(2)–Li(2)–O(3), 110.1(4); Li(2)–O(2)–Li(3), 129.7(4); O(1)–Li(3)–O(2), 112.1(4); Li(1)–O(3)–Li(2), 129.2(4).

hydrogen atoms and NMe groups. However, the solution ¹H NMR spectrum of **1** at 20 °C shows equivalent NMe groups and equivalent methylene hydrogens, i.e. there is a fast fluxionality which causes an inversion of absolute configuration of the nitrogen atoms.† We believe this fluxionality is based on lithium–nitrogen dissociation–association processes such as those reported in, for example, 2,6-bis[(dimethylamino)methyl]phenyllithium.⁸

When three equivalents of LiI are added to a benzene solution of **1**, at 20 °C, a lithium iodide adduct **2** is obtained in a clean reaction. Complex **2** was obtained after crystallization from a pentane-layered benzene solution as colourless, moisture-sensitive crystals, and preliminary microanalytical data suggested it to be the 1 : 1 Li(OAr) : LiI species. With ¹H NMR spectroscopy one can discern two inequivalent but coordinated (dimethylamino)methyl groups, i.e. **2** is at least a dinuclear species with two inequivalent lithium atoms.§ To elucidate the degree of association of **2** and to have proof for the tertiary amine coordination, we have carried out an X-ray structure determination.‡ The crystal structure of **2** involves

‡ Crystal data for **1**: [LiOC₆H₂(CH₂NMe₂)₂-2,6-Me-4]₃, C₃₉H₆₃N₆O₃Li₃, *M* = 684.79, a plate-shaped yellowish crystal (0.12 × 0.37 × 0.75 mm), monoclinic, space group *P*2₁/*n*, with *a* = 42.381(5), *b* = 8.8417(11), *c* = 11.1802(10) Å, β = 90.539(8)°, *V* = 4189.2(8) Å³, *Z* = 4, *D*_c = 1.086 g cm⁻³, *F*(000) = 1488, μ(Mo-Kα) = 0.6 cm⁻¹; 9515 reflections (0.48 < θ < 25.38°; ω–2θ scan; *T* = 100 K) were measured on an Enraf-Nonius CAD4 diffractometer using Zr-filtered Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz-polarization effects. The structure was solved using direct methods (SHELXS86) and refined by full-matrix least-squares techniques on *F* (SHELX76) to an *R*-value of 0.068, *R*_w = 0.059, *w*⁻¹ = [σ²(*F*)] for 4106 reflections with *I* ≥ 2.5 σ(*I*) and 610 parameters. Twenty H atoms were introduced at calculated positions and refined riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were refined using three common isotropic thermal parameters.

Crystal data for **2**: [Li₂{OC₆H₂(CH₂NMe₂)₂-2,6-Me-4}I]₂, C₂₆H₄₂N₄O₂Li₄I₂, *M* = 724.22, a yellowish crystal (0.18 × 0.20 × 0.35 mm), monoclinic spacegroup, *I*2/*c*, with *a* = 17.112(1), *b* = 8.952(2), *c* = 22.049(4) Å, β = 93.92(1)°, *V* = 3369.7(10) Å³, *Z* = 4, *D*_c = 1.428 g cm⁻³, *F*(000) = 1440, μ(Mo-Kα) = 18.7 cm⁻¹; 10031 reflections (θ < 27.5°; ω–2θ scan; *T* = 300 K) were measured on an Enraf-Nonius CAD4T diffractometer using monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz-polarization effects, and for absorption (DIFABS; correction range 0.62–1.40). The structure was solved using Patterson techniques (SHELXS86) and refined by full-matrix least-squares techniques on *F* (SHELX76) to an *R*-value of 0.051, *R*_w = 0.050, *w*⁻¹ = [σ²(*F*)] for 2871 reflections with *I* ≥ 2.5 σ(*I*) and 202 parameters. Eighteen H atoms were introduced at calculated positions and refined riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Analytical data for **2**: ¹H NMR (C₆D₆, 300 MHz, 298 K): δ 6.74 (s, 2H, *meta*-H); 4.30, 4.03 (dd, 2H, ²*J*_{H,H} = 10.9 Hz, CH₂N); 2.53, 2.45 (dd, 2H, ²*J*_{H,H} = 9.2 Hz, CH₂N); 2.41, 1.94, 1.84, 1.78 (4s, 12H, NMe); 2.18 (s, 3H, *para*-Me). Calc. for C₂₆H₄₂I₂Li₄N₄O₂·½C₆H₆: C, 44.8; H, 5.9; N, 7.5. Found: C, 44.65; H, 5.95; N, 7.5%.

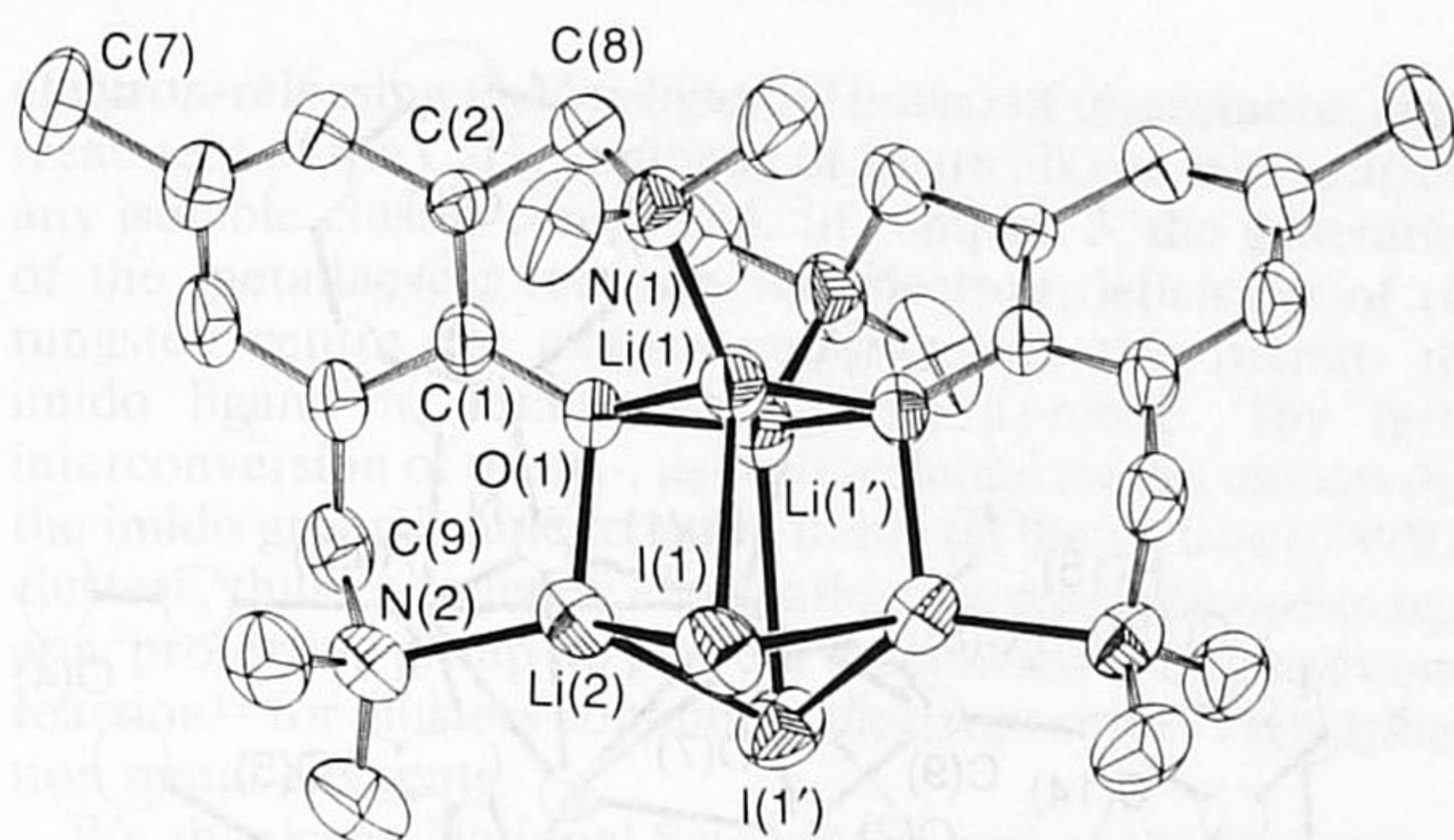


Fig. 2 Molecular structure of $[\text{Li}_2\{\text{OC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,6-Me-4}\}\text{I}]_2$, **2**; ORTEP drawing with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Li(1)–O(1), 1.917(9); Li(1')–O(1), 1.903(7); Li(2)–O(1), 1.934(9); Li(1)–N(1), 1.999(9); Li(2)–N(2), 1.983(10); Li(1)–I(1), 2.814(8); Li(2)–I(1), 2.738(9); Li(2)–I(1'), 2.829(9); O(1)–C(1), 1.355(5); Li(1)–O(1)–Li(2), 95.2(4); Li(1')–O(1)–Li(2), 95.8(4); Li(1)–O(1)–Li(1'), 83.4(3).

the packing of four discrete $\text{Li}_4(\text{OAr})_2\text{I}_2$ clusters in the unit cell. The molecular structure of **2**, which possesses a twofold rotation axis, is shown in Fig. 2.

Complex **2** is a tetranuclear species, which is most easily described as a distorted Li_4 tetrahedron with the two iodide atoms and the two oxygen atoms of the phenolate ligands coordinating above the four Li_3 faces. The four tertiary amine substituents are all coordinated to different lithium atoms which thereby acquire a tetrahedral coordination sphere, two with an $\text{I}_2\text{O}_2\text{N}$ environment and two with an $\text{I}_2\text{O}_2\text{N}$ environment [Li(1) and Li(2), respectively]. Chemically the structure can be seen as a dimer of two lithium phenolate units each of which contains one molecule of LiI caught by a coordinating amine group.

The Li–O and $C_{\text{ipso}}\text{–O}$ distances of 1.918(9) (average) and 1.355(5) Å, respectively, are significantly longer than those in **1**, but are comparable with those reported earlier for lithium

phenolates and enolates.^{5,6} These results emphasize the unusual nature, *i.e.* 'quasi-aromaticity' of trimeric **1**.

The molecular structures of **1** and **2** nicely demonstrate the potential of phenolate ligands with tertiary amine substituents to coordinate to more than one metal centre, and to stabilize unusual aggregates. The application of this type of bis-*ortho*-chelating phenolate as a ligand for early transition and lanthanide metals is currently being studied.

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Synthesis and Structural Characterization of a Novel WRu_2 Cluster Compound Possessing a Terminal Phenylimido Ligand

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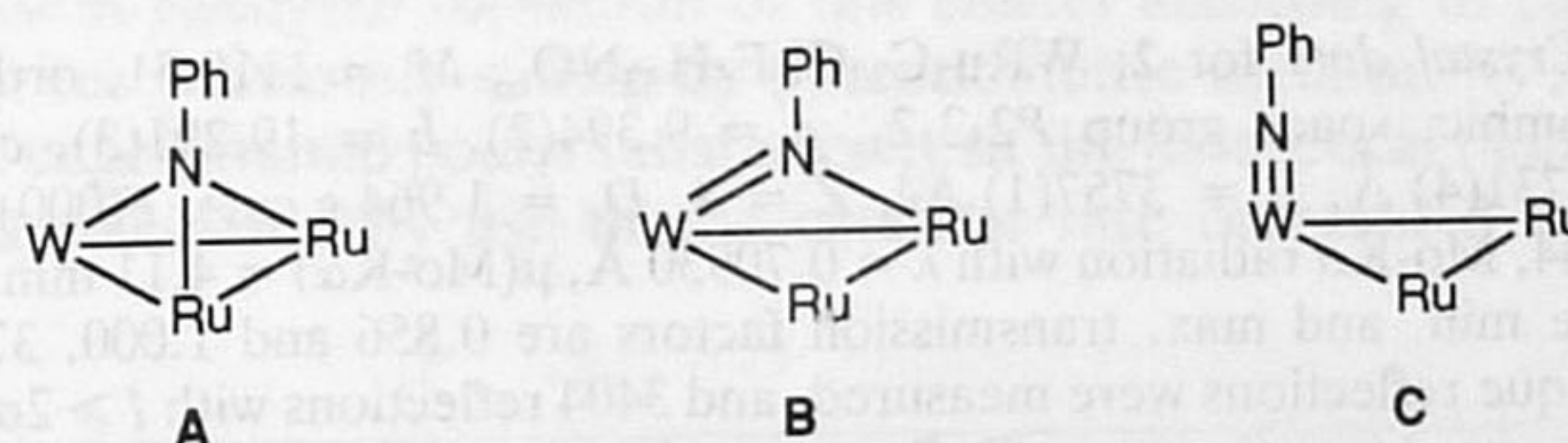
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Cluster complex $[\text{WRu}_2(\text{C}_5\text{Me}_5)(\text{CO})_6(\text{NPh})\{\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)\}]$ **2**, which possesses a novel terminal phenylimido ligand, has been prepared by treatment of phenylimido cluster $[\text{WRu}_2(\text{C}_5\text{Me}_5)(\text{CO})_7(\mu_3\text{-NPh})(\text{CF}_3\text{CCHCF}_3)]$ **1** with hex-3-yne, whereas the respective reaction with dimethyl acetylenedicarboxylate afforded $[\text{WRu}_2(\text{C}_5\text{Me}_5)(\text{CO})_6(\mu_3\text{-NPh})\{\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)\}]$ **3** containing a regular face-bridging imido ligand; complexes **2** and **3** have been examined by single-crystal X-ray diffraction.

There is considerable interest in the chemistry of cluster compounds containing an imido functional group.¹ The imido group is generally associated with the metal core *via* a typical μ_3 -mode¹ or a less common μ_4 -mode.² The μ_3 -mode was also observed in WRu_2 cluster compounds, suggesting that the imido ligand has a tendency to interact with the metal skeleton *via* two M–N sigma bonds and an M←N dative bond (mode A).³ We are unaware of any example in which the imido ligand is coordinated to only one metal atom *via* a metal–nitrogen triple-bond (mode C), although a few examples of the asymmetric $\text{W}=\text{N}(\text{Ph})\rightarrow\text{Ru}$ mode in the related WRu_2 system (mode B)⁴ and the terminal mode in dinuclear complexes⁵ have been documented. Now, we report the preparation and structural identification of the first example of mode C.

Treatment of the phenylimido complex $[\text{WRu}_2(\text{C}_5\text{Me}_5)(\text{CO})_7(\mu_3\text{-NPh})(\text{CF}_3\text{CCHCF}_3)]$ ^{3b} **1** with an excess of hex-3-yne in refluxing toluene (100 °C, 30 min) afforded an alkyne–alkenyl coupling product $[\text{WRu}_2(\text{C}_5\text{Me}_5)(\text{CO})_6(\text{NPh})\{\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3)\}]$ **2** (46%). The formula was



Scheme 1