evaporation of the solvent. A similar procedure was used to prepare X-ray quality crystals of **1a** that contain D-H_2pheHA.

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[9] Elemental analysis calcd for $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_{2.5}$ (**1**): C 33.99, H 3.49, N 11.45, Cu 19.98; found: C 33.97, H 3.53, N 11.30, Cu 18.9. ESMS (methanol): m/z: 1482.8 $[M{\cdot}2NO_3]^+$.

[10] Crystal data for **1**: $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_8$, $M_r = 1689.18$, tetragonal, space group $P4_1$ (no. 76), $a = 19.310(2)$, $b = 19.310(2)$, $c = 18.330(3)$, $\alpha = 90.000$, $\beta = 90.000$, $\gamma = 90.000°$, $V = 6835.0(15)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.641$ g cm^{-1}; $2.98 < \theta < 26.50°$; crystal dimensions, $0.24 \times 0.34 \times 0.40$ mm; $\mu = 24.52$ cm^{-1}; $T = 133(2)$ K; 14015 unique of 60540 reflections collected. 14015 reflections and 784 parameters were used for the full-matrix, least-squares refinement on F^2, $R1 = 0.0560$, and $wR2 = 0.1543$. A PLATON/SQUEEZE subroutine (Spek, A. L. Platon, *Acta Crystallogr. Sect. A* **1990**, *46*, C-34) was used to handle solvent and anion disorder. Further details are given in the Supporting Information.

[11] Elemental analysis calcd for **1a** $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_{4.5}$: C 33.24, H 3.66, N 11.20, Cu 19.54; found: C 33.19, H 3.69, N 11.04, Cu 19.2. ESMS (methanol): m/z: 1482.8 $[M{\cdot}2NO_3]^+$.

[12] Crystal data for **1a**: $[C_{45}H_{50}N_{10}O_{10}Cu_5Sm](NO_3)_3(H_2O)_{12}$, $M_r = 1761.22$, tetragonal, space group $P4_3$ (no. 78), $a = 19.253(3)$, $b = 19.253(3)$, $c = 18.313(4)$, $\alpha = 90.000$, $\beta = 90.000$, $\gamma = 90.000°$, $V = 6788(2)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.723$ g cm^{-1}; $2.99 < \theta < 28.35°$; crystal dimensions(mm), $0.20 \times 0.24 \times 0.42$; $\mu = 24.82$ cm^{-1}; $T = 133(2)$ K; 16835 unique of 77985 reflections collected. 16835 reflections and 784 parameters were used for the full-matrix, least-squares refinement on F^2, $R1 = 0.0387$, $wR2 = 0.1025$. A PLATON/SQUEEZE subroutine (Spek) was used to handle solvent and anion disorder. Further details are given in the Supporting Information. CCDC-192390 (**1**) and CCDC-192391 (**1a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Novel Synthetic Approach to Trinuclear 3d-4f Complexes: Specific Exchange of the Central Metal of a Trinuclear Zinc(II) Complex of a Tetraoxime Ligand with a Lanthanide(III) Ion**

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Salen (*N*,*N*′-disalicylideneethylenediamine) and its analogues are fascinating and versatile ligands because their metal complexes are known to serve as catalysts of organic reactions,[1] models of catalytic centers of metalloenzymes,[2] and nonlinear optical materials.[3] The negatively charged oxygen atoms of the transition-metal complexes of the salen-type ligands can coordinate to a different cation such as an alkali metal,[4] an alkaline-earth metal,[5] a d-block transition metal,[6] or an f-block transition metal[7] to provide a number of attractive heteronuclear complexes. In particular, synthesis and characterization of heterodinuclear complexes bearing 3d and 4f transition metals are interesting and important because magnetic superexchange interactions between the bridged metal atoms may exist in the complexes.[8,9]

A variety of acyclic and cyclic "compartmental ligands" bearing two different sites have also been designed to synthesize such a heteronuclear complex.[10] However, preparation of the complexes is limited mostly to stepwise reactions using a readily available mononuclear complex. The method of the strategy can be regarded as an "addition reaction". In recent years, advanced synthetic methodology for these types of heteronuclear complexes has been developed. For example, the metal initially bound to one site of some ligands migrates to another site during the second metalation step.[11] Metal exchange between two "coordination-position isomers" of a heterodinuclear complex has also been reported.[12] Here we describe a new method—a "substitution reaction"—to synthesize a $(3d)_2(4f)$ trinuclear complex. A $(3d)_3$ homotrinuclear complex generated in a cooperative manner from three zinc(II) ions and acyclic tetraoxime ligand **1** bearing two salen-type chelating moieties[13] under-

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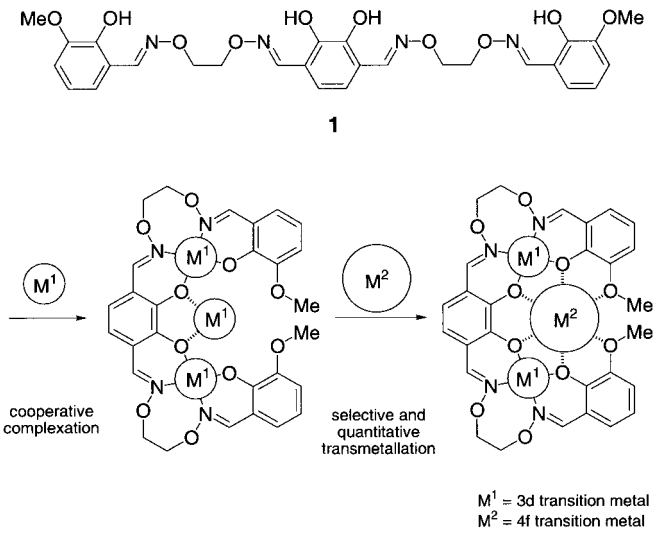
goes exclusive and quantitative transmetalation of the central 3d metal ion with a 4f metal ion.

When **1** reacts with two equivalents of 3d transition metal ions the linear form of **1** changes into a C-shaped one to give a cavity surrounded by the six oxygen atoms (Scheme 1). The complex is expected to have a high affinity toward metal cations, since the donor atoms are arranged in a cyclic fashion and negatively charged.



Scheme 1. A novel synthetic approach to a $(3d)_2(4f)$ heterotrinuclear complex via a $(3d)_3$ homonuclear complex.

Addition of a solution of zinc(II) acetate to a solution of **1**[14] (H_4L) resulted in the solution changing from colorless to yellow and the appearance of a new band (332 nm) in the UV/Vis spectrum (Figure 1). Although **1** has two chelating moieties, spectroscopic titration of **1** and zinc(II) acetate clearly indicated the exclusive formation of the 1:3 complex $[LZn_3]^{2+}$ (inset of Figure 1). Formation of other complexes with a different stoichiometry is ruled out because of the observed spectroscopic changes having three isosbestic points (256, 286, and 322 nm). This interesting and high cooperativity was also observed in the ^{1}H NMR spectroscopic titration.[14]

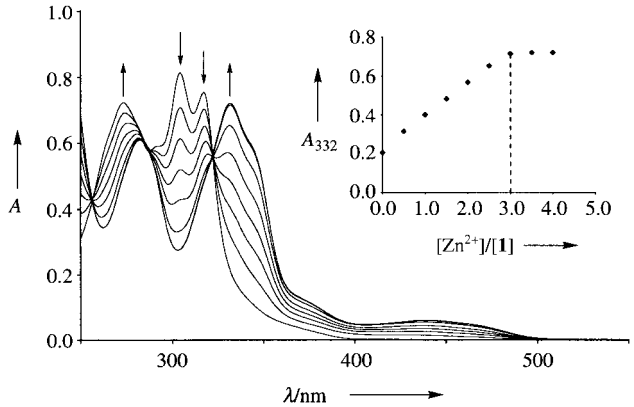


Figure 1. UV/Vis spectral changes of **1** on addition of zinc(II) acetate ($CHCl_3/CH_3OH$ (1/1), $[\mathbf{1}] = 2.0 \times 10^{-4}$ M). The inset shows the plot of absorbance at 332 nm against the molar ratio of $[Zn^{2+}]/[\mathbf{1}]$.

The structure of the 1:3 complex $[LZn_3]^{2+}$ in the crystalline state was determined by X-ray crystallography using a single crystal of $[LZn_3(OAc)_2(EtOH)]$ (Figure 2).[15] The complex

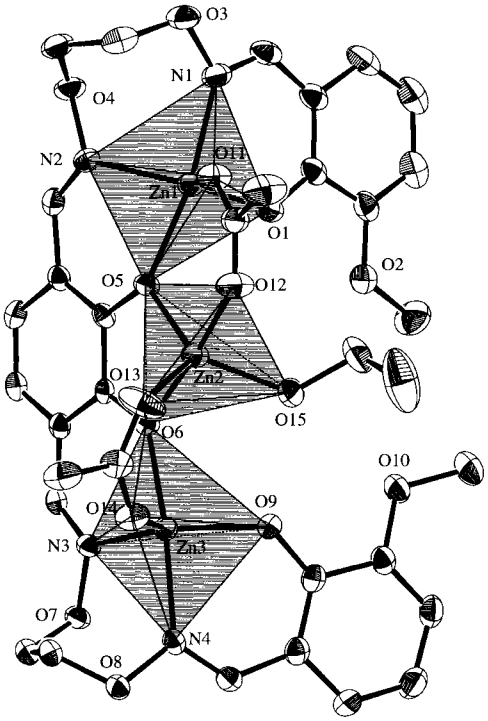


Figure 2. Crystal structure of the trinuclear zinc(II) complex $[LZn_3(OAc)_2(EtOH)]$. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å]: Zn1-O1 1.922(3), Zn1-O5 2.077(3), Zn1-O11 1.982(3), Zn1-N1 2.137(3), Zn1-N2 2.151(3), Zn2-O5 2.023(3), Zn2-O6 2.059(3), Zn2-O12 1.995(3), Zn2-O13 2.009(3), Zn2-O15 2.001(3), Zn3-O6 2.041(3), Zn3-O9 1.964(3), Zn3-O14 1.999(3), Zn3-N3 2.072(3), Zn3-N4 2.149(3).

$[LZn_3]^{2+}$ has three zinc atoms arranged in a trigonal bipyramidal geometry. The two salamo (H_2salamo: 1,2-bis(salicylideneaminooxy)ethane) moieties provide the N_2O_2 donor set to the two outer zinc atoms (Zn1 and Zn3), while the oxygen atoms (O5 and O6) of the central catechol moiety coordinate to all three zinc atoms. In addition, the two μ-acetato ligands link Zn1 to Zn2 and Zn2 to Zn3. Although the central metal (Zn2) was located in the cavity, four of the six oxygen atoms (O1, O2, O9, and O10) arranged along the rim of the cavity do not coordinate to Zn2. Deprotonated ligand **1** is expected to bind to Zn2 more weakly than Zn1 and Zn3, because only two donor atoms of **1** coordinate to Zn2. Namely, it would be expected that the central Zn2 ion would be replaced more easily with another metal ion possessing a larger radius and coordination number suitable for the O_6 cavity than Zn1 and Zn3. Thus, we utilized $[LZn_3]^{2+}$ to synthesize novel heteronuclear $(3d)_2(4f)$ complexes.

Treatment of a solution of $[LZn_3]^{2+}$ with lanthanide(III) ions resulted in a hypsochromic shift in the absorption spectra. A typical example of the titration of $[LZn_3]^{2+}$ with $Ln(NO_3)_3$ is shown in Figure 3 (Ln = Eu). The absorption band at 370 nm (shoulder) arising from the formation of a new species increased while a concomitant decrease in the absorption band at 440 nm of $[LZn_3]^{2+}$ was observed. Isosbestic points

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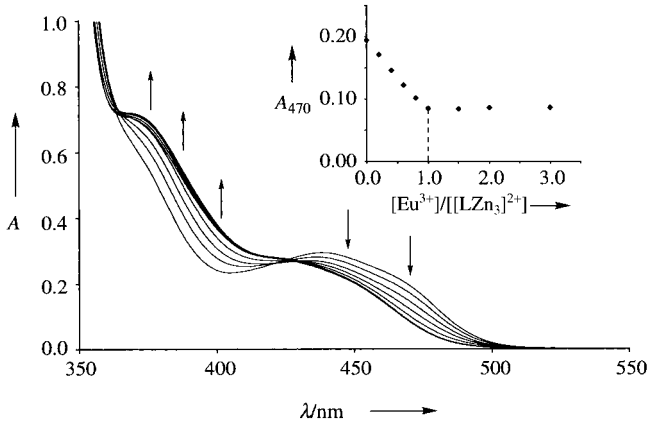

Figure 3. UV/Vis spectral changes of $[LZn_3]^{2+}$ on addition of europium(III) nitrate ($CHCl_3/CH_3OH$ (1/1), $[[LZn_3]^{2+}] = 1.0 \times 10^{-4}$ M). The inset shows the plot of absorbance at 470 nm against the molar ratio of $[Eu^{3+}]/[[LZn_3]^{2+}]$.

were evident at 426 and 364 nm. The spectral changes are completed by the addition of just one equivalent of Ln^{3+} ions (inset of Figure 3), which indicates the formation of the expected species $[LZn_2Ln]^{3+}$. The stoichiometry was also supported by ^1H NMR spectroscopic measurements.[14]

The formation of the heterotrinuclear complex was further confirmed by ESI mass spectroscopic analysis of $[LZn_3(OAc)_2]$ in the presence of one equivalent of $Eu(NO_3)_3$. Intense peaks at m/z 977.0 and 460.0 and the isotope distribution in the spectrum indicate the existence of $[LZn_2Eu(OAc)_2]^+$ and $[LZn_2Eu(OAc)]^{2+}$, respectively. One equivalent of Zn^{2+} ions was apparently liberated from the complex to give $[LZn_2Eu(OAc)_2]^+$, since no peak attributed to the homonuclear species $[LZn_3]^{2+}$ was observed.

Yellow single crystals were obtained from a solution of $[LZn_3]^{2+}$ containing one equivalent of $Eu(NO_3)_3$. X-ray crystallographic analysis[16] reveals that the crystals correspond to a heterotrinuclear complex containing a trinuclear Zn-Eu-Zn core bridged by the phenolate oxygen atoms of the ligand and μ-acetato ligands (Figure 4). The two zinc atoms (Zn1 and Zn2) have an octahedral and a square-pyramidal environment, respectively, in which the four equatorial positions are occupied by the N_2O_2 donor sets of the salamo moieties. The europium atom, with a nonacoordinate geometry, is located in the pseudo cavity consisting of the six oxygen atoms of the ligand. The distances between the europium atom (Eu1) and the six donor atoms (O1, O2, O5, O6, O9, and O10) range from 2.380 to 2.614 Å, which suggests there is effective incorporation of the europium(III) ion (Figure 5). Consequently, the ligand wraps around the europium atom and results in a helical complex in which the terminal benzene rings lie close to each other.

Very interestingly, a mixture of **1** with excess zinc(II) and europium(III) ions (four and three equivalents, respectively) gave spectra identical to that of $[Zn_2Eu(OAc)_2]^+$. The zinc(II) ions, thus, bind selectively to the two salamo moieties and the europium(III) ion in the central cavity. This selective uptake of two zinc(II) ions and one europium(III) ion can be attributed to the fact that the cavity size and shape of the two different sites fit more suitably to the ionic radius, the coordination geometry, and the coordination number of these ions. Hence,

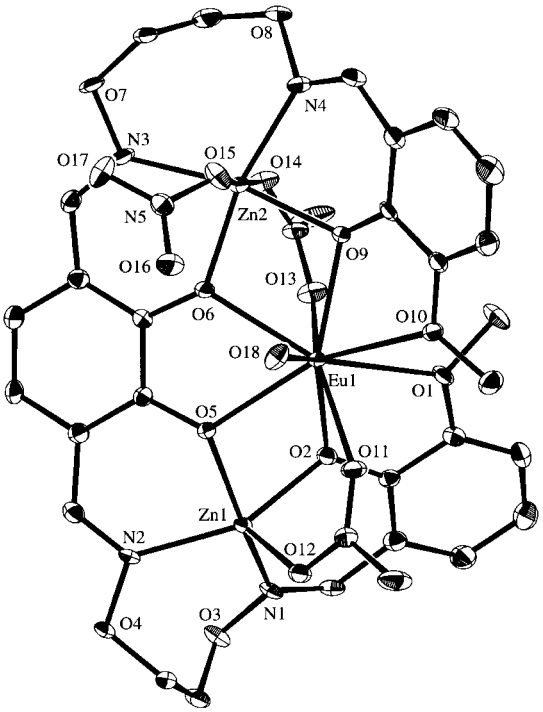

Figure 4. ORTEP drawing (30% probability level) of the trinuclear complex $[LZn_2Eu(OAc)_2(NO_3)(H_2O)]$. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å]: Eu1-O1 2.594(3), Eu1-O2 2.435(2), Eu1-O5 2.380(2), Eu1-O6 2.385(2), Eu1-O9 2.384(2), Eu1-O10 2.614(3), Eu1-O11 2.372(3), Eu1-O13 2.457(3), Eu1-O18 2.412(3), Zn1-O2 2.045(2), Zn1-O5 1.995(2), Zn1-O12 1.991(3), Zn1-N1 2.071(3), Zn1-N2 2.109(3), Zn2-O6 2.017(2), Zn2-O9 2.090(2), Zn2-O14 2.088(3), Zn2-O15 2.201(3), Zn2-N3 2.179(3), Zn2-N4 2.136(3).

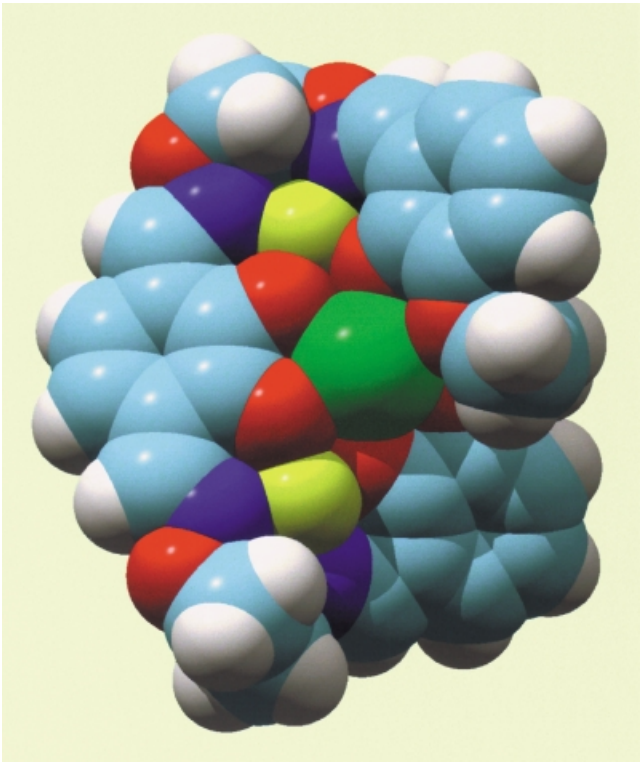

Figure 5. Space-filling representation of $[LZn_2Eu]^{3+}$. Anions and the water molecule coordinating to the metal atoms have been omitted for clarity.

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the heteronuclear complex containing the lanthanide atom is stabilized to a greater extent than the homotrinulcear zinc(II) complex. As a result, only the central zinc ion of the homo complex formed initially is replaced quantitatively by the lanthanide(III) ion.

We believe that this facile and effective strategy to synthesize helical or cyclic heteronuclear complexes will open a new way to construct various functionalized coordination systems

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[14] For the synthesis of **1** as well as ^{1}H NMR titration experiments, see the Supporting Information.

[15] Crystallographic data for $[LZn_3(OAc)_2(EtOH)]\cdot 0.5\,EtOH\cdot 0.5\,CHCl_3$ ($C_{35.5}H_{41.5}Cl_{1.5}N_4O_{15.5}Zn_3$, $M_r = 1021.51$): monoclinic, space group $P2_1/n$ (no. 14), $a = 10.6324(15)$, $b = 23.665(2)$, $c = 16.371(2)$ Å, $\beta = 103.8170(5)°$, $V = 4000.2(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.696$ g cm^{-3}, $T = 120$ K, Rigaku Mercury CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), $\mu = 1.961$ mm^{-1}, collected reflections 23 896, of which 6981 were unique ($R_{int} = 0.0596$), $2\theta_{max} = 50.00°$, $R1 = 0.0425$ ($I > 2\sigma(I)$), $wR2 = 0.1143$ (all data).[17,18]

[16] Crystallographic data for $[LZn_2Eu(OAc)_2(NO_3)]\cdot 3.5\,Me_2CO$ ($C_{42.5}H_{55}EuN_5O_{21.5}Zn_2$, $M_r = 1262.61$): triclinic, space group $P\bar{1}$ (no. 2), $a = 12.987(5)$, $b = 13.475(4)$, $c = 14.808(5)$ Å, $\alpha = 73.201(9)$, $\beta = 87.921(11)$, $\gamma = 84.247(10)°$, $V = 2468.3(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.699$ g cm^{-3}, $T = 120$ K, Rigaku Mercury CCD diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), $\mu = 2.304$ mm^{-1}, collected reflections 17 507, of which 9389 were unique ($R_{int} = 0.0254$), $2\theta_{max} = 52.00°$, $R1 = 0.0342$ ($I > 2\sigma(I)$), $wR2 = 0.0818$ (all data).[17,18]

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[18] CCDC-187146 and CCDC-187147 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The Structure of Neutral Proline**

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The conformational behavior of amino acids is of critical importance to understand the dynamic role of these molecules in protein or polypeptide formation.[1] Consequently, extensive structural research has been conducted on amino acids in their natural solid-state phase. This point is worth noting because solid amino acids present a zwitterionic structure in the solid state (i.e. a bipolar, ionized form of the type $^+H_3N{-}CH(R){-}COO^-$), which does not occur in the polypeptide chain.[2] To obtain the structure of the neutral form of amino acids, research should be conducted in the gas phase, in an atmosphere that is essentially free of intermolecular interactions with other partners. In particular, the collisionless environment of a supersonic jet[3] seems particularly well adapted for such studies. The obvious difficulties of experimental studies in the gas phase are caused by the high melting points and associated low vapor pressures of amino acids. Classical heating methods were employed for the analysis of the only two amino acids that have been studied to date in the gas phase, glycine[4] and alanine[5]. As an alternative, laser ablation offers an advantageous way of vaporizing solid organic compounds,[6] in which the fast desorption produced by the energy of a laser pulse prevents the thermal decomposition caused by the heating methods. Despite the extensive use of laser ablation with mass-spectrometry techniques,[7] few groups have explored the possibility of combining laser ablation with the high resolution of rotational spectroscopy. Suenram et al.[8] and Walker and Gerry[9] independently developed two laser-ablation devices, mostly devoted to investigate the rotational spectra of metal oxides and halides. The first was also applied in the structural study of glycine in the gas phase, but it was reported that the classical heating method was more reliable.[10]

In this context we have configured a new experiment in which a laser-ablation system especially constructed for solid organic compounds is combined with Fourier-transform (FT) microwave spectroscopy in a supersonic jet, to allow the structural characterization of the vaporized species in the gas phase. The ablation nozzle is accommodated at the back side of one mirror of the Fabry–Pérot resonator, close to the resonator axis (Figure 1). An oil diffusion pump, backed by a roots blower, evacuates the chamber. Laser ablation is produced by the second harmonic ($\lambda = 532$ nm) of a pulsed

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