4–**6**: $HBF_4\cdot Et_2O$ (0.1 mL) was added to a solution of **2** (0.20 g, 0.35 mmol) in Et_2O (30 mL). The reaction mixture was stirred for 5 min to give an orange solid, which was collected by filtration, washed with Et_2O, and dried under vacuum to give **3** (0.15 g, 67%). Complex **3** (0.20 g, 0.31 mmol) was dissolved in CH_2Cl_2 (2 mL), which was then layered with diethyl ether (10 mL). The mixture was allowed to stand for a week to give a brown solution and brown-red needles of **4**, which were collected by filtration, washed with hexane (5 mL), and dried under vacuum (0.080 g, 40% based on Ru). The mother liquor was evaporated to dryness, and hexane (10 mL) was added to give a brown-yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum to give **6** (0.076 g, 38% based on Ru). The filtrate was concentrated to dryness, and the residue purified by column chromatography (silica gel, eluent: hexane) to give **5** as a colorless oil (0.015 g, 8% based on Ru). **4**: ^1H NMR (300.13 MHz, $[D_6]$acetone): $\delta = -13.51$ (d, $J(H,H) = 1.38$ Hz, 1H, RuH), 1.40 (d, $J(H,H) = 5.37$ Hz, 3H, CH_3), 1.91 (s, 15H, Cp*), 1.93 (s, 15H, Cp*), 2.39 (s, 15H, Cp*), 4.06 (qd, $J(H,H) = 5.73$, 1.38 Hz, 1H, Ru-C*H*-CH_3), 5.26 (d, $J(H,H) = 5.37$ Hz, 1H, =CH), 5.46 (dd, $J(H,H) = 7.23$, 4.95 Hz, 1H, =CH), 7.13 (t, $J(H,H) = 5.13$ Hz, 1H, =CH), 8.20 (d, $J(H,H) = 7.23$ Hz, 1H, =CH); $^{13}C\{^1H\}$ NMR (75.48 MHz, $[D_6]$acetone): $\delta = 9.64$ (s, Cp*), 9.75 (s, Cp*), 10.10 (s, Cp*), 24.36 (s, CH_3), 37.42 (s, =CH), 41.52 (s, Ru*C*HCH_3), 54.02 (s, =CH), 64.83 (s, =CH), 92.48 (s, Cp*), 106.20 (s, 2Cp*), 146.89 (s, =CHRu), 168.32 (s, =CRu); elemental analysis (%) calcd for $C_{37}H_{54}B_2F_8Ru_3$: C 45.55, H 5.58; found: C 45.80, H 5.62. **5**: ^1H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.16$ (t, $J(H,H) = 7.5$ Hz, 3H, CH_3), 1.99 (s, 15H, Cp*), 2.20 (q, $J(H,H) = 7.5$ Hz, 2H, CH_2), 4.15 (s, 4H, Cp); $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): $\delta = 11.74$ (s, Cp*), 14.63 (s, CH_3), 20.81 (s, CH_2), 71.81 (s, Cp), 71.91 (s, Cp), 84.32 (s, Cp*), 92.13 (s, Cp); MS (CI): m/z (%): 330 (100) $[M^+]$. **6**: ^1H NMR (300.13 MHz, CD_2Cl_2): $\delta = 1.23$ (t, $J(H,H) = 7.6$ Hz, 3H, CH_3), 1.93 (s, 30H, Cp*), 2.63 (q, $J(H,H) = 7.6$ Hz, 2H, CH_2), 4.12 (s, 2H, Cp), 4.27 (s, 2H, Cp); $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2): $\delta = 10.46$ (s, Cp*), 10.94 (s, CH_3), 19.84 (s, CH_2), 55.17 (s, Cp), 56.29 (s, Cp), 76.20 (s, Cp), 86.49 (s, Cp*); elemental analysis (%) calcd for $C_{27}H_{39}BF_4Ru_2$: C 49.70, H 6.02; found: C 50.02, H 5.86.

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[12] Crystal data for **4**: $C_{37}H_{54}B_2F_8Ru_3$, $M_r = 975.63$; triclinic, space group $P\bar{1}$; $a = 9.3162(12)$, $b = 11.6864(15)$, $c = 18.106(2)$ Å, $\alpha = 78.518(3)$, $\beta = 87.415(3)$, $\gamma = 80.060(3)^\circ$, $V = 1902.7(4)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.703$ g cm^{-3}; 12561 reflections, 8468 independent reflections ($R_{int} = 0.0571$); $R_1 = 0.0560$, $wR_2 = 0.1104$ for 527 parameters and 4100 reflections with $I > 2\sigma(I)$. Crystals of **4** suitable for X-ray diffraction were grown from a solution in CH_2Cl_2 layered with diethyl ether. Intensity data were collected on a Bruker SMART CCD Area Detector with graphite-monochromated $Mo_{K\alpha}$ radiation at room temperature. The structure was solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on F^2 by using the Bruker SHELXTL (Version 5.10) program package. All non-hydrogen atoms were refined anisotropically. The two BF_4^- counteranions were highly disordered, and their atomic distances (B–F, F$\cdots$F) were constrained during the structural refinement. The metal-bound hydrido ligand H1 was located in the difference Fourier map and refined with isotropic thermal parameter. The remaining hydrogen atoms were placed in ideal positions and refined with a riding model. CCDC-173137 contains 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).

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Synthesis, Structure, and Molecular Orbital Calculations of Chromium(III) and Iron(III) Complexes Containing η^2-Pyrazolato Ligands[**]

Karl R. Gust, John E. Knox, Mary Jane Heeg,
H. Bernhard Schlegel, and Charles H. Winter[*]

The coordination chemistry of pyrazolato ligands has been extensively explored, particularly among complexes of the mid to late transition metals.[1] Among the 1656 Group 6–11 complexes containing pyrazolato ligands whose structures

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[*] Prof. Dr. C. H. Winter, K. R. Gust, J. E. Knox, Dr. M. J. Heeg,
Prof. Dr. H. B. Schlegel
Department of Chemistry
Wayne State University
Detroit, Michigan 48202 (USA)
Fax: (+1) 313-577-1377
E-mail: chw@chem.wayne.edu

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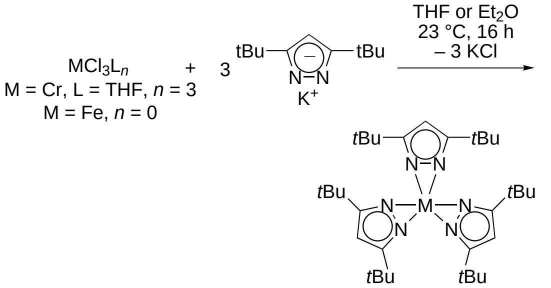
have been deposited in the Cambridge Crystallographic Database to date (version 5.21; April 2001), coordination modes have been limited to η^1 and μ-η^1:η^1, with the exception of our η^5-pyrazolato complex of ruthenium.[2] Until recently, η^2 coordination of pyrazolato ligands was extremely rare outside of lanthanide and actinide complexes.[1, 3, 4] Since 1997, we have reported many early transition metal complexes containing η^2-pyrazolato ligands.[5, 6] In addition, main group element complexes with η^2-pyrazolato ligands have been reported in the past several years.[7–12] A significant open question relates to the occurrence of η^2-pyrazolato ligands among transition metal complexes with partially filled d shells, where repulsions between the filled d orbitals and pyrazolato nitrogen atoms might destabilize η^2-pyrazolato coordination in favor of other coordination modes. Mösch-Zanetti has reported the synthesis and structure of tris(3,5-di-*tert*-butylpyrazolato)titanium(III) and several other titanium(III) pyrazolato complexes, and found η^2 coordination of the pyrazolato ligands in these d^1 systems.[13] However, there have been no reports of η^2-pyrazolato ligand coordination among the complexes of the Group 4–11 metals with d^2 or higher electronic configurations. Herein, we report the synthesis and characterization of tris(3,5-di-*tert*-butylpyrazolato)chromium(III) and tris(3,5-di-*tert*-butylpyrazolato)iron(III). These complexes contain η^2-pyrazolato ligands, and establish that η^2 coordination is possible despite the d^3 and d^5 configurations. We have also carried out molecular orbital calculations on model chromium(III) and iron(III) pyrazolato complexes. While theory predicts that η^2-pyrazolato ligands are more stable than η^1-pyrazolato ligands for chromium(III), the opposite trend is found for iron(III). The observation of a stable iron(III) η^2-pyrazolato complex suggests that the steric bulk of the substituents in the 3- and 5-positions of the pyrazolato ligands plays a pivotal role in stabilizing η^2-pyrazolato ligands relative to other coordination modes.

Treatment of trichlorotris(tetrahydrofuran)chromium(III) or iron(III) chloride (1 equiv) with potassium 3,5-di-*tert*-butylpyrazolate[8] (3 equiv) in tetrahydrofuran or diethyl ether led to the formation of tris(3,5-di-*tert*-butylpyrazolato)chromium(III) (**1**, 66%) and tris(3,5-di-*tert*-butylpyrazolato)iron(III) (**2**, 22%) as deep purple and orange-red crystals, respectively, after crystallization from hexane [Eq. (1)]. The structures of **1** and **2** were established by a combination of spectroscopic and analytical techniques, and by X-ray crystal structure determinations. Both complexes are paramagnetic and show only very broad singlets in the ^{1}H NMR spectra.



1, M = Cr, 66%
2, M = Fe, 22%

(1)

EPR spectra of **1** and **2** were recorded in a toluene glass at 5 K. Both complexes exhibit spectra consistent with high-spin, octahedral metal ions.[14] The EPR spectra of **1** and **2** are virtually identical to spectra previously reported for high-spin, octahedral tris(2-trimethylsilyamidopyridinato)chromium(III)[15a] and the analogous axially symmetric iron(III) complex.[15b] The magnetic moment for **1** was found to be $\mu_{\text{eff}} = 3.43\,\mu_B$, which is close to the spin-only magnetic moment expected for three unpaired electrons ($3.87\,\mu_B$). For **2**, $\mu_{\text{eff}} = 6.10\,\mu_B$, which is close to the spin-only magnetic moment expected for five unpaired electrons ($5.92\,\mu_B$).

Complex **1** exists in the solid state as a monomeric complex with three η^2-pyrazolato ligands (Figure 1).[16] The pyrazolato ligands are canted slightly away from perfect trigonal-prismatic geometry toward a three-bladed propeller. The pyrazolato ligands are coordinated to the chromium atom with nearly perfect η^2 geometry, with Cr–N bond lengths ranging from 1.956(6) to 1.986(6) Å. The N-Cr-N angles within each η^2-pyrazolato ligand are also very similar, and vary from 40.24(11) to 40.51(11)°. The structural parameters of **1** are very similar to those reported for tris(η^2-3,5-di-*tert*-butylpyrazolato)aluminum,[9] tris(η^2-3,5-di-*tert*-butylpyrazolato)scandium,[11] and tris(η^2-3,5-di-*tert*-butylpyrazolato)titanium.[13] The crystal structure of $\mathbf{2}\cdot(C_6H_{14})_{0.5}$ was also determined, and the structural parameters are very similar to those of **1**. Crystals of $\mathbf{2}\cdot(C_6H_{14})_{0.5}$ were only solved with inclusion of twinning parameters and will be discussed in a later publication.

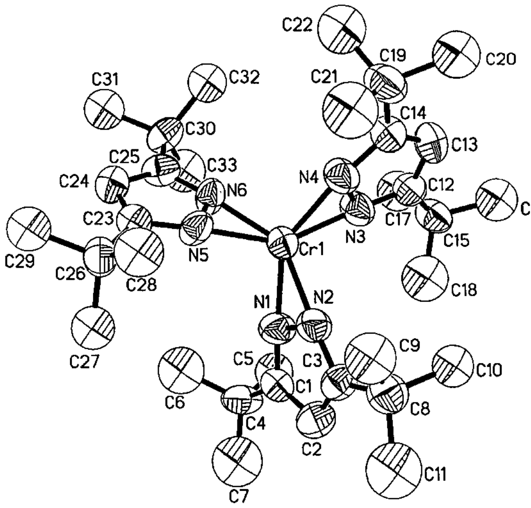
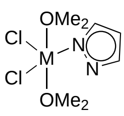
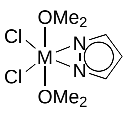


Figure 1. Perspective view of **1**. Selected bond lengths [Å] and angles [°]: Cr1-N1 1.978(3), Cr1-N2 1.981(3), Cr1-N3 1.963(3), Cr1-N4 1.985(3), Cr1-N5 1.983(3), Cr1-N6 1.978(3), N1-N2 1.362(4), N3-N4 1.366(4), N5-N6 1.371(4); N1-Cr1-N2 40.24(11), N3-Cr1-N4 40.50(11), N5-Cr1-N6 40.51(11), N1-Cr1-N3 109.91(13), N1-Cr1-N4 143.05(13), N1-Cr1-N5 100.05(13), N1-Cr1-N6 112.76(12), N2-Cr1-N3 99.62(13), N2-Cr1-N4 111.44(13), N2-Cr1-N5 111.55(13), N2-Cr1-N6 145.15(13), N3-Cr1-N5 147.50(13), N3-Cr1-N6 112.90(13), N4-Cr1-N5 115.17(13), N4-Cr1-N6 101.63(13), Cr1-N1-N2 70.01(19), Cr1-N2-N1 69.75(18), Cr1-N3-N4 70.60(19), Cr1-N4-N3 68.90(18), Cr1-N5-N6 69.53(18), Cr1-N6-N5 69.95(18).

To gain insight into the preference of η^1 versus η^2 bonding, ab initio calculations were performed on the simplified model



3a, M = Cr
4a, M = Fe



3b, M = Cr
4b, M = Fe

complexes **3** and **4** at the B3LYP/6-311G* level of theory.[18, 19] The optimized structures of **3b** and **4b** are in good agreement with the X-ray crystal structure data (Cr–N(calcd) = 2.03, 2.02 versus Cr–N(X-ray) = 1.956(6) – 1.986(6) Å; Fe–N(calcd) = 2.06, 2.06 versus Fe–N(X-ray) = 2.008(2), 2.009(2) Å).

The charge on the pyrazolato ligand in **3b** was −0.58 and was −0.65 in **4b** (natural population analysis[20]), making the nitrogen–metal bonding slightly more ionic than in titanium(IV) complexes that we have previously reported.[5] Similar to our previous molecular orbital studies of titanium(IV) complexes,[5] η^2 bonding occurred through interaction of molecular orbitals containing symmetric and antisymmetric combination of the nitrogen lone pairs with the empty hybridized 3d and 4s orbitals, as depicted in Figure 2 for **4b**. Consequently, **3b** is 6.6 kcal mol^{-1} more stable than **3a**. In high-spin **4**, all five d orbitals formally are singly occupied and are significantly lower in energy than the nitrogen lone pair orbitals, resulting in very little orbital interaction. One of the orbitals containing the symmetric combination of the nitrogen lone pairs forms an antibonding interaction with a d orbital on iron, but the other orbitals have minimal interaction with the iron atom. Due to this change in the orbital interaction, η^2-pyrazolato bonding in **4** is weakened relative to that in **3**. By contrast, the nitrogen lone pair in the **4a** interacts with the 3d and 4s orbitals on iron, stabilizing **4a** by 1.9 kcal mol^{-1} relative to **4b**.

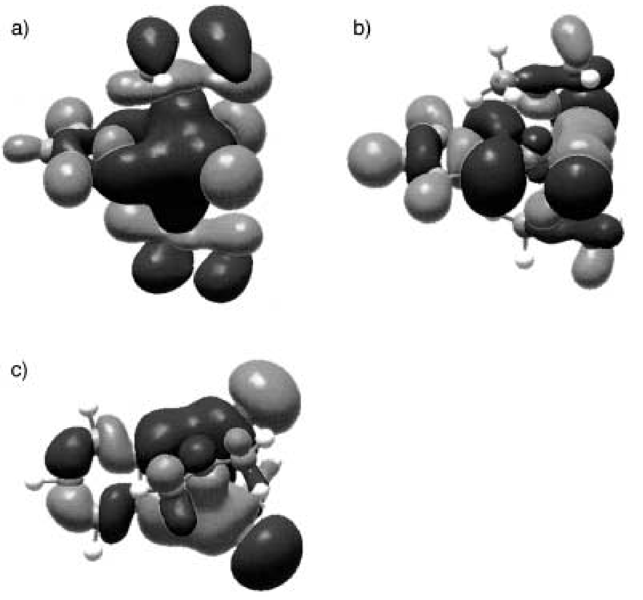


Figure 2. Calculated molecular orbitals showing a) symmetric lone pair of **4b**, b) symmetric lone pair of **4b**, and c) antisymmetric lone pair of **4b**.

The crystal structures of **1** and **2** document the first examples of η^2-pyrazolato ligand coordination in complexes of metal ions with d^2 or higher electronic configurations. The results of the molecular orbital calculations on **3** and **4** demonstrate that, in the absence of steric effects, η^2 coordination becomes less stable than η^1 at the d^5 configuration of iron(III). Consistent with our theoretical model, pyrazolato complexes of the mid to late d-block metals have exhibited either η^1- or μ-η^1:η^1-pyrazolato coordination modes.[1] As specific relevant examples, bis(pyrazolato)iron(II)[21, 22] and tris(pyrazolato)iron(III)[22] are polymeric with μ,η^1:η^1-pyrazolato ligands.[23] Based upon our results, we predict that octahedral homoleptic pyrazolato complexes with d^5 or higher electronic configurations will not exhibit η^2-pyrazolato ligands *in the absence of steric effects*. However, the 3,5-di-*tert*-butylpyrazolato ligand and other pyrazolato ligands with bulky substituents may lead to η^2 bonding in metal complexes with high d-electron counts. We note that the 3,5-di-*tert*-butylpyrazolato ligand has seen very little use in the coordination chemistry of the mid to late d-block metals. The present work implies that this ligand and related azolato ligands containing bulky substituents may exhibit much different coordination chemistry than azolato ligands substituted with hydrogen, small hydrocarbon groups, or other moieties with small steric profiles.

Experimental Section

1: A 100-mL Schlenk flask was charged with trichlorotris(tetrahydrofuran)chromium(III) (0.500 g, 1.33 mmol), 3,5-di-*tert*-butylpyrazolatopotassium (1.166 g, 5.34 mmol), and tetrahydrofuran (50 mL). After the mixture had been stirred for 16 h at ambient temperature, the solvent was removed under reduced pressure to yield a purple solid. This solid was extracted with hexane (50 mL) and the resultant solution was filtered through a 2-cm pad of Celite on a coarse glass frit. The deep purple filtrate was placed in a −20 °C freezer for 36 h to afford **1** as deep purple crystals (0.521 g, 66 %): m.p. 252 °C (decomp); IR (Nujol): $\tilde{\nu}$ = 1570 (w), 1515 (m), 1361 (s), 1309 (m), 1241 (s), 1207 (w), 1116 (w), 1011 (m), 1003 (m), 790 (s), 714 (m) cm^{-1}; ^{1}H NMR (C_6D_6, 22 °C): δ = 2.89 (br. s, $C(CH_3)_3$); elemental analysis (%) calcd for $C_{33}H_{57}CrN_6$: C 67.20, H 9.74, N 14.25; found: C 67.00, H 9.74, N 14.25.

2: In a fashion similar to the preparation of **1**, iron(III) chloride (0.318 g, 1.96 mmol) was treated with 3,5-di-*tert*-butylpyrazolatopotassium (1.500 g, 6.87 mmol) in diethyl ether (50 mL) to afford **2** as orange-red crystals (0.250 g, 22 % yield): m.p. 229 °C (decomp); IR (Nujol): $\tilde{\nu}$ = 1516 (m), 1363 (s), 1291 (w), 1251 (m), 1228 (s), 1204 (m), 1013 (w), 980 (m), 796 (s), 711 (m) cm^{-1}; ^{1}H NMR (C_6D_6, 22 °C): δ = 6.38 (br. s, $C(CH_3)_3$); elemental analysis (%) calcd for $C_{33}H_{57}FeN_6$: C 66.76, H 9.68, N 14.16; found: C 66.70, H 9.54, N 14.26.

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[16] X-ray crystal data for **1**: $C_{36}H_{63}CrN_6$, $M_r = 589.85$, triclinic, $P\bar{1}$, $a = 9.9754(17)$, $b = 12.707(2)$, $c = 16.687(3)$ Å, $\alpha = 77.228(3)$, $\beta = 75.734(3)$, $\gamma = 70.655(4)^\circ$, $V = 1911.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.025$ g cm^{-3}, $\mu = 0.326$ mm^{-1}, 8755 independent reflections harvested from 2450 frames of data collected at 20 s per frame and 0.2° between frames yielded 13711 integrated intensities, $R_{int} = 0.029$. All data were included in the refinement. For $I > 2\sigma(I)$, $R_1 = 0.0685$ and $wR_2 = 0.1856$; including weak data $R_1 = 0.1585$ and $wR_2 = 0.2141$. Siemens/Bruker P4-CCD, $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å), graphite monochromator, $2\Theta_{max} = 56.5^\circ$, $T = 295(2)$ K. Suitable crystals for single-crystal X-ray analysis were selected and mounted inside thin-walled capillaries in a dry box under nitrogen atmosphere. Data collection and integration used the Bruker SMART and SAINT software. Empirical absorption corrections were calculated using the program SADABS.[17] Solution and refinement used the programs SHELXS[17] and SHELXL-93.[17] All non-hydrogen atoms were described anisotropically. Hydrogen atoms were placed in calculated positions. The 3,5-di-*tert*-butylpyrazolato ligands typically show severe disorder in the *tert*-butyl groups, which results in modeling difficulties and high *R* values. However, other criteria of chemical and crystallographic reasonableness show these to be acceptable structural models. CCDC-175570 (**1**) and CCDC-175571 ($\mathbf{2} \cdot (C_6H_{14})_{0.5}$) 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).

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Hexagonal and Cubic Thermally Stable Mesoporous Tin(IV) Phosphates with Acidic and Catalytic Properties[**]

Christian Serre,[*] Aline Auroux, Antonella Gervasini, Maryvonne Hervieu, and Gérard Férey

Since the initial work of Mobil researchers on the synthesis of mesoporous silica,[1] a lot of work has been devoted to extend the composition of mesoporous materials to metal oxides other than silica for applications in acid, redox catalysis, or photocatalytic processes.[2–4]

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[*] Dr. C. Serre, Prof. Dr. G. Férey
Institut Lavoisier, UMR CNRS 8637
Université de Versailles St-Quentin en Yvelines
45 Avenue des Etats-Unis, 78035 Versailles Cedex (France)
Fax: (+33) 1-3925-4358
E-mail: serre@chimie.uvsq.fr

Dr. A. Auroux
Institut de Recherches sur la Catalyse, CNRS
2 avenue Einstein, 69626 VILLEURBANNE Cedex (France)

Dr. A. Gervasini
Dipartimento di Chimica Fisica ed Electrochimica
Università degli Studi di Milano
via C. Golgi 19, 20133 Milano (Italy)

Prof. Dr. M. Hervieu
CRISMAT, ISMRA, UMR CNRS 6508
6 Boulevard du Maréchal Juin, 14050 Caen (France)

[**] Dr. F. Taulelle and C. Lorentz (Laboratoire Chimie et RMN du solide, Université Louis Pasteur, Strasbourg, France) and Prof. J. C. Dumas (LAMMI, Université Montpellier II, Montpellier, France) are gratefully acknowledged for their collaboration in NMR and Mössbauer experiments.