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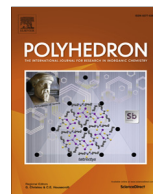


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Synthesis of a sulfonate substituted β -diketimine ligand and its complexes of Co(II), Ni(II), Zn(II) and Pd(II)

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ABSTRACT

Deprotonation of the β -diketimine ligand $[\text{CH}_2(\text{C}(\text{Me})=\text{N}-2,6\text{-diisopropylphenyl})_2]$ using $n\text{-BuLi}$ followed by treatment with SO_3NMe_3 afforded the sulfonate substituted β -diketimine ligand $\text{Li}(\text{THF})_2[\text{O}_3\text{SCH}(\text{C}(\text{Me})=\text{N}-2,6\text{-diisopropylphenyl})_2]$ (**1**). Compound **1** is moderately soluble in water. It reacts with Ni(II) and Zn(II) chlorides to produce $[\text{LMCl}]$ complexes ($\text{L} = \mathbf{1}$ without $\text{Li}(\text{THF})_2$), in which the ligand coordinates to the metal in a tripodal fashion. Metal nitrate complexes $[\text{LM}(\text{O}_2\text{NO})]$ [$\text{M} = \text{Co(II), Ni(II) and Zn(II)}$] were also synthesized and structurally characterized. The reaction of **1** with $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ was also explored. Depending on the reaction conditions, two dinuclear Pd complexes, $[\text{LPdCl}_2\text{PdCl}_2]^-$ and $[\text{LPdCl}_2\text{PdL}]$, were formed. In both the cases the sulfonate group remained uncoordinated.

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1. Introduction

The monoanionic bidentate β -diketiminate (NacNac) ligands have emerged as one of the most versatile ligands in coordination chemistry. They have been utilized in stabilizing a wide variety of transition metals, main group elements and lanthanide metals [1–9]. Incorporation of ligating groups into these ligands not only provides additional binding modes but also changes the physical properties, such as solubility. However, these kinds of modifications in β -diketiminate ligands are less explored in coordination chemistry. Ligating groups like $-\text{CN}$, $-\text{NO}_2$, $-\text{PPh}_2$, N -aryloxy, N -(hydroxyaryl), N -(thioalkoxyaryl), N -pendant amine and $-\text{NHAr}$ are integrated into the β -diketimine ligands resulting in the variation of their coordination mode and/or their donor ability [10–32]. Making β -diketiminate ligands water soluble would further increase their potential as supporting ligands. With this view, we designed a β -diketimine ligand bearing an $-\text{SO}_3^-$ group and synthesized $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ (Fig. 1) and its various metal complexes. The results of these reactions are reported herein.

2. Experimental

2.1. General considerations

All reactions and manipulations involving air/moisture sensitive compounds were carried out under an N_2 atmosphere using

a Schlenk line and a glove box. $\text{MCl}_2\cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Ni, Co and Cu}$) and $\text{M}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Zn, Ni and Co}$) were procured from Himedia Laboratories and used as received. $[\text{ZnCl}_2(\text{CH}_3\text{CN})_2]$ [33] and $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ [34] were prepared by following literature procedures. Toluene, hexane and THF were distilled from $\text{Na/benzophenone ketyl}$ as and when required. Acetonitrile was distilled from CaH_2 . Benzene- d_6 was condensed from $\text{Na/benzophenone ketyl}$ and CDCl_3 was condensed from CaH_2 and stored in a glove box. Acetone- d_6 was dried over molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. Elemental analyses were performed using a Flash 2000 organic elemental analyzer. IR spectra were recorded on a Smart Omni Transmission analyzer. Thermogravimetric analyses were performed on a SDT Q600V20.9 Build 20 instrument.

2.2. Single crystal X-ray experiments

Data collection for all the compounds was done on an OXFORD XCALIBUR diffractometer, equipped with a CCD area detector, using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation and a low temperature device. In order to avoid quality degradation, all the single crystals were coated with perfluoropolyalkyl ether oil/paraffin oil and mounted on a glass fiber using cyanoacrylate glue. All calculations were performed using SHELXS-97 and SHELXL-97 [35]. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). All non-hydrogen atoms in the crystals were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was

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included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks. All the datasets were collected to 2θ values $> 50^\circ$. Relevant data concerning crystallographic data, data collection and refinement details are summarised in Table 1.

2.3. Synthesis of $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ (**1**)

To a solution of NacNacH (2.29 g, 5.48 mmol) in THF (20 mL) was added $n\text{-BuLi}$ (3.7 mL, 1.6 M in hexane, 5.92 mmol) slowly at -78°C , followed by stirring for one hour. The resultant mixture was cannulated into a Schlenk flask containing a suspension of $\text{SO}_3\cdot\text{NMe}_3$ (0.84 g, 6.04 mmol) in THF (20 mL) at -78°C . The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was filtered using Celite; the volume of the filtrate was reduced to 20 mL and kept at 0°C to obtain colourless $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ (**1**) Crystals. Yield: 2.84 g, 80%. Mp: $215\text{--}216^\circ\text{C}$. ^1H NMR (CD_3OD , 400 MHz, ppm) δ : 7.11 (6H, m, ArH), 5.09 (1H, s, $\gamma\text{-CH}$), 3.76 (8H, m, THF), 3.08 (4H, m, CHMe_2), 2.13 (6H, s, $\alpha\text{-Me}$), 1.89 (8H, m, THF), 1.14 (24H, m, CHMe_2). ^{13}C NMR (CD_3OD , 100 MHz, ppm) δ : 170.75, 146.30, 138.38, 138.32, 125.23, 124.15, 124.02, 82.14, 68.87, 28.57, 28.48, 26.51, 24.58, 24.50, 24.10, 23.52, 20.64. IR (KBr, cm^{-1}) ν : 1050 (vs, $\nu(\text{S}=\text{O})$), 628 (m, $\nu(\text{C}=\text{S})$).

2.4. Reactions of $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ with metal chlorides

2.4.1. In aqueous medium

With $[\text{NiCl}_2\cdot 6\text{H}_2\text{O}]$: To a mixture of $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ (0.20 g, 0.31 mmol) and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.08 g, 0.34 mmol) was added water

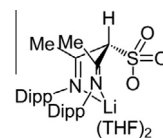


Fig. 1. $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$.

(15 mL) in a 50 mL round bottom flask. The resultant mixture was stirred for 12 h to afford an off-white precipitate and filtered through a frit. The precipitate was washed with water ($10\text{ mL} \times 2$) and dried under vacuum. The crude product was dissolved in THF (10 mL) and kept at room temperature to obtain colourless crystals in a moderate yield. These crystals were found to be the β -diketiminium bisulfate salt $[\text{CH}(\text{C}(\text{Me})=\text{NHDipp})_2][\text{HSO}_4]$ (**2**). ^1H NMR (CDCl_3 , 400 MHz, ppm) δ : 12.01 (2H, s, NH), 7.37 (6H, m, ArH), 3.10 (4H, m, CHMe_2), 2.10 (6H, s, $\alpha\text{-Me}$), 1.25 (24H, t, CHMe_2).

A similar procedure was used for the reactions with other metal chlorides (Cu(II), Co(II) and Zn(II)) with $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ in aqueous medium. The β -diketiminium bisulfate was formed in all cases.

2.4.2. In organic solvents

With $[\text{ZnCl}_2(\text{CH}_3\text{CN})_2]$: To a mixture of $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ (0.20 g, 0.31 mmol) and $[\text{ZnCl}_2(\text{CH}_3\text{CN})_2]$ (0.07 g, 0.32 mmol) was added THF (10 mL) in a 50 mL Schlenk flask. The resultant mixture was refluxed under a nitrogen atmosphere for 12 h and allowed to cool to room temperature, filtered through a frit, and then the volatiles were removed from the filtrate under vacuum. The crude product was dissolved in hot toluene and kept at room temperature to

Table 1
Crystal data and structure refinement parameters for compounds **2–5** and **7–9**.

Compound	2 ·THF	3 · $\frac{1}{2}$ Toluene	4 · CH_3CN	5 · $3\text{CH}_2\text{Cl}_2$	7 · CH_3CN	8 · CH_3CN	9 · CH_3CN
Empirical formula	$\text{C}_{33}\text{H}_{52}\text{N}_2\text{O}_5\text{S}$	$\text{C}_{65}\text{H}_{90}\text{Cl}_2\text{N}_4\text{O}_6\text{S}_2\text{Zn}_2$	$\text{C}_{33}\text{H}_{47}\text{ClN}_4\text{NiO}_3\text{S}$	$\text{C}_{61}\text{H}_{90}\text{Cl}_{10}\text{N}_4\text{O}_3\text{Pd}_2\text{S}$	$\text{C}_{33}\text{H}_{47}\text{N}_5\text{O}_6\text{SZn}$	$\text{C}_{33}\text{H}_{47}\text{N}_5\text{NiO}_6\text{S}$	$\text{C}_{33}\text{H}_{47}\text{CoN}_5\text{O}_6\text{S}$
Formula weight	588.83	1289.17	673.97	1526.73	707.19	700.53	700.75
Crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic	triclinic
<i>T</i> (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
<i>a</i> (Å)	17.6035(3)	27.530(3)	10.0210(3)	15.9409(3)	17.0819(7)	16.1883(8)	9.9943(3)
<i>b</i> (Å)	18.3194(3)	18.8528(6)	12.0069(4)	16.6802(3)	11.7913(3)	13.1403(5)	11.8217(4)
<i>c</i> (Å)	19.3040(3)	14.633(2)	16.0509(5)	16.7560(3)	19.5109(7)	17.5304(10)	16.7399(4)
α (°)	62.774(2)	90.00	101.389(3)	60.206(2)	90.00	90.00	102.249(2)
β (°)	70.396(2)	118.805(18)	99.856(3)	69.7452(18)	114.322(5)	105.081(5)	97.665(2)
γ (°)	73.091(2)	90.00	107.017(3)	86.6039(17)	90.00	90.00	108.752(3)
<i>V</i> (Å ³)	5144.11(15)	6655.1(12)	1755.51(10)	3592.39(11)	3581.0(2)	3600.6(3)	1786.24(9)
<i>Z</i>	6	4	2	2	4	4	2
<i>D</i> _{calc} (Mg m^{-3})	1.140	1.287	1.275	1.411	1.312	1.292	1.303
μ (mm^{-1})	0.134	0.915	0.725	0.945	0.792	0.645	0.587
<i>F</i> (000)	1920.0	2728.0	716.0	1572.0	1496.0	1488.0	742.0
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$	$0.30 \times 0.25 \times 0.25$	$0.30 \times 0.20 \times 0.20$	$0.31 \times 0.24 \times 0.20$	$0.38 \times 0.32 \times 0.28$	$0.30 \times 0.30 \times 0.25$	$0.40 \times 0.30 \times 0.30$
θ range (°)	2.72–25.00	2.68–25.00	3.93–25.00	2.75–25.00	2.68–29.23	3.78–29.17	2.64–29.33
No. of collected/	57890/18102	15881/5877	21858/6126	40683/12623	18274/8336	38182/8738	23595/8514
Unique reflections	(<i>R</i> (int) = 0.0473)	(<i>R</i> (int) = 0.0318)	(<i>R</i> (int) = 0.0236)	(<i>R</i> (int) = 0.0450)	(<i>R</i> (int) = 0.0366)	(<i>R</i> (int) = 0.0589)	(<i>R</i> (int) = 0.0375)
No. of data/restraints/params	18102/1/1143	5877/0/378	6126/0/400	12623/2/754	8336/0/427	8738/0/431	8514/0/427
Goodness-of-fit (GOF) on <i>F</i> ²	1.045	1.045	1.076	1.048	0.996	1.037	1.047
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> $> 2\sigma(I)$) ^a	0.0691, 0.1837	0.0312, 0.0738	0.0303, 0.0785	0.0536, 0.1295	0.0363, 0.0814	0.0525, 0.0976	0.0373, 0.0882
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.1027, 0.2112	0.0409, 0.0794	0.0357, 0.0824	0.0726, 0.1435	0.0584, 0.0882	0.0894, 0.1081	0.0476, 0.0937
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e Å^{-3})	1.13 and −0.85	0.38 and −0.35	0.30 and −0.29	2.37 and −2.30	0.43 and −0.46	0.77 and −0.72	0.42 and −0.37

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

obtain colourless [NacNacSO₃ZnCl] (**3**) crystals. Even after drying the crystals under high vacuum for several hours, toluene could not be removed completely from crystals. Yield: 0.14 g, 70%. Mp: 167–168 °C dec. ¹H NMR (C₆D₆, 400 MHz, ppm) δ: 7.06 (4H, m, ArH), 6.95 (2H, m, ArH), 5.39 (1H, s, β-CH), 3.58 (2H, m, CHMe₂), 2.53 (2H, m, CHMe₂), 1.84 (6H, s, α-Me), 1.39 (6H, d, *J* = 6.8 Hz, CHMeMe), 1.27 (6H, d, *J* = 6.8 Hz, CHMeMe), 1.17 (6H, d, *J* = 6.8 Hz, CHMeMe), 0.87 (6H, d, *J* = 6.8 Hz, CHMeMe). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ: 179.17, 142.28, 139.53, 138.66, 129.34, 125.79, 124.10, 71.89, 29.29, 27.54, 25.51, 24.86, 24.61, 24.15, 24.04. IR (KBr, cm⁻¹) ν: 1022 (m, ν(S–O)), 661 (m, ν(C–S)).

With [NiCl₂·6H₂O]: To a mixture of NacNacSO₃Li·2THF (0.21 g, 0.32 mmol) and NiCl₂·6H₂O (0.08 g, 0.34 mmol) was added CH₃CN (15 mL) in a 50 mL Schlenk flask. The resultant mixture was stirred for 24 h and then filtered through a frit. The volume of the filtrate was reduced to 10 mL under vacuum and kept at –20 °C to obtain green coloured crystals of [NacNacSO₃NiCl] (**4**). The crystals were dried under high vacuum to yield the complex without acetonitrile. Yield: 0.10 g, 52%. Mp: 228–229 °C dec. *Anal.* Calc. for C₂₉H₄₁ClN₂O₃SNi: C, 58.85; H, 6.98; N, 4.73. Found: C, 58.68; H, 6.72; N, 4.84%. IR (KBr, cm⁻¹) ν: 1013 (m, ν(S–O)), 662 (m, ν(C–S)).

With [PdCl₂(CH₃CN)₂] in dichloromethane: To a stirred solution of [PdCl₂(CH₃CN)₂] (0.09 g, 0.35 mmol) in dichloromethane (10 mL) was added dropwise a solution of NacNacSO₃Li (0.21 g, 0.32 mmol) in dichloromethane (10 mL) at room temperature. The resultant mixture was stirred for 18 h to obtain an orange precipitate, which was filtered through a frit. The precipitate was washed with dichloromethane and dried under vacuum. The crude material was recrystallized from a mixture of dichloromethane and acetone at room temperature to obtain orange crystals (**5**). Yield: 0.22 g, 51%. Mp: 231–232 °C dec. In the following NMR data, [NacNacSO₃Pd₂Cl₄][–] is represented by **a** and [NacNacH₂]⁺ is represented by **b**. ¹H NMR (acetone-*d*₆, 400 MHz, ppm) δ: 9.81 (2H, s, NH) (**b**), 7.29 (6H, m, ArH) (**b**), 7.15 (6H, m, ArH) (**a**), 5.76 (1H, s, β-CH) (**a**), 4.55 (1H, s, β-CH) (**b**), 3.99 (2H, m, CHMe₂) (**a**), 3.54 (2H, m, CHMe₂) (**a**), 2.98 (6H, s, α-Me) (**b**), 2.82 (4H, m, CHMe₂) (**b**), 2.28 (6H, s, α-Me) (**a**), 1.74 (6H, d, *J* = 6.8 Hz, CHMeMe) (**a**), 1.30 (6H, d, *J* = 6.8 Hz, CHMeMe) (**a**), 1.22 (6H, d, *J* = 6.8 Hz, CHMeMe) (**a**), 1.15 (6H, d, *J* = 6.8 Hz, CHMeMe) (**a**), 1.07 (12H, d, *J* = 6.8 Hz, CHMeMe) (**b**), 0.93 (12H, d, *J* = 6.8 Hz, CHMeMe) (**b**). The ¹³C NMR spectrum could not be recorded due to the poor solubility of the compound in common deuterated solvents. IR (KBr, cm⁻¹) ν: 1034 (s, ν(S–O)), 630 (s, ν(C–S)).

With [PdCl₂(CH₃CN)₂] in acetonitrile: To a stirred solution of [PdCl₂(CH₃CN)₂] (0.04 g, 0.15 mmol) in acetonitrile (10 mL) was added dropwise a solution of NacNacSO₃Li (0.10 g, 0.15 mmol) in acetonitrile (10 mL) at room temperature. The resultant mixture was stirred for 18 h and then filtered through a frit. The filtrate was evaporated under vacuum and washed with dichloromethane to remove any unreacted ligand. Attempts to grow single crystals were unsuccessful. Yield: 0.12 g, 61%. Mp: 224–225 °C dec. ¹H NMR acetone-*d*₆, 400 MHz, ppm) δ: 7.10 (6H, m, ArH), 5.58 (1H, s, β-CH), 4.01 (2H, m, CHMe₂), 3.45 (2H, m, CHMe₂), 2.18 (6H, s, α-Me), 1.53 (6H, d, *J* = 6.8 Hz, CHMeMe), 1.30 (6H, d, *J* = 6.4 Hz, CHMeMe), 1.17 (6H, d, *J* = 7.2 Hz, CHMeMe), 1.13 (6H, d, *J* = 6.8 Hz, CHMeMe). The ¹³C NMR spectrum could not be recorded due to the poor solubility of the compound in common deuterated solvents. *Anal.* Calc. for C₅₈H₈₂Cl₂N₄O₆S₂Pd₂: C, 54.46; H, 6.46; N, 4.38. Found: C, 54.32; H, 6.35; N, 4.32%. IR (KBr, cm⁻¹) ν: 1033 (m, ν(S–O)), 627 (m, ν(C–S)).

2.5. General procedure for the synthesis of metal nitrate complexes

An equimolar mixture of NacNacSO₃Li·2THF and M(NO₃)₂·6H₂O was taken in a 50 mL Schlenk flask. Acetonitrile (~15 mL) was condensed onto the mixture at liquid nitrogen temperature, the

reaction mixture was warmed slowly to room temperature and stirred for 12 h. The resultant suspension was filtered through a frit. The volume of the filtrate was reduced to 10 mL and kept at –20 °C to obtain crystals in almost quantitative yield.

With [Zn(NO₃)₂·6H₂O]: NacNacSO₃Li (0.21 g, 0.32 mmol) and Zn(NO₃)₂·6H₂O (0.10 g, 0.34 mmol). White crystals of [NacNacSO₃Zn(O₂NO)] (**7**) were obtained. The crystals were dried under high vacuum to obtain the complex without acetonitrile. Mp: 138–139 °C dec. ¹H NMR (CDCl₃/acetone-*d*₆, 400 MHz, ppm) δ: 7.20 (6H, m, ArH), 5.50 (1H, s, β-CH), 3.15 (2H, m, CHMe₂), 2.57 (2H, m, CHMe₂), 2.29 (6H, s, α-Me), 1.16 (24H, m, CHMeMe). ¹³C NMR (CDCl₃, 100 MHz, ppm) δ: 178.79, 141.70, 139.25, 138.81, 128.39, 125.45, 124.27, 71.64, 29.16, 27.29, 26.24, 24.46, 24.32, 24.23. *Anal.* Calc. for C₂₉H₄₁N₃O₆SZn: C, 55.72; H, 6.61; N, 6.72. Found: C, 55.89; H, 6.72; N, 6.81%. IR (KBr, cm⁻¹) ν: 1008 (s, ν(S–O)), 661 (s, ν(C–S)).

With [Ni(NO₃)₂·6H₂O]: NacNacSO₃Li (0.20 g, 0.31 mmol) and Ni(NO₃)₂·6H₂O (0.09 g, 0.31 mmol). Blue coloured crystals of [NacNacSO₃Ni(O₂NO)] (**8**) were obtained. The crystals were dried under high vacuum to obtain the complex without acetonitrile. Mp: 143–144 °C dec. *Anal.* Calc. for C₂₉H₄₁N₃O₆SNi: C, 56.32; H, 6.68; N, 6.79. Found: C, 56.24; H, 6.54; N, 6.96%. IR (KBr, cm⁻¹) ν: 1017 (vs ν(S–O)), 661 (s, ν(C–S)).

With [Co(NO₃)₂·6H₂O]: NacNacSO₃Li (0.22 g, 0.34 mmol) and Co(NO₃)₂·6H₂O (0.10 g, 0.34 mmol). Pink coloured crystals of [NacNacSO₃Co(O₂NO)] (**9**) were obtained. The crystals were dried under high vacuum to obtain the complex without acetonitrile. Mp: 116–117 °C dec. *Anal.* Calc. for C₂₉H₄₁N₃O₆SCo: C, 56.30; H, 6.68; N, 6.79. Found: C, 56.23; H, 6.57; N, 6.68%. IR (KBr, cm⁻¹) ν: 1016 (s, ν(S–O)), 660 (s, ν(C–S)).

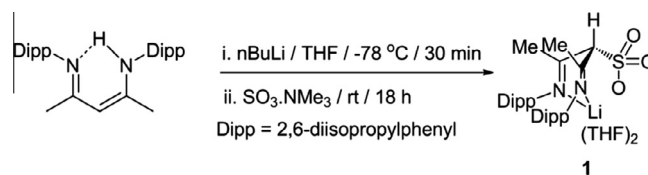
3. Results and discussion

3.1. Synthesis of the NacNacSO₃Li·2THF ligand

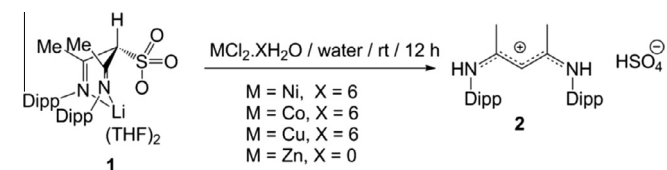
It has been reported in the literature that an –SO₃[–] group was introduced into the tripodal ligand tris(1-pyrazolyl)methane by treating it with *n*-BuLi followed by SO₃NMe₃ in THF [36]. This procedure was adopted to incorporate an –SO₃[–] group into NacNacH at the central carbon (γ position). Deprotonation of NacNacH with *n*-BuLi followed by treatment with SO₃NMe₃ (Scheme 1) afforded NacNacSO₃Li·2THF (**1**) in good yield. The compound was characterized by IR and ¹H NMR spectroscopy. The IR spectrum showed bands associated with ν(S–O) and ν(C–S) at 1050 and 628 cm⁻¹ respectively. The ¹H NMR spectrum confirmed the presence of two THF molecules in the ligand. Diffraction quality crystals could not be obtained for single crystal X-ray diffraction studies. The compound showed moderate solubility in water.

3.2. Reactions of NacNacSO₃Li·2THF with metal chlorides in water (metal = Zn^{II}, Ni^{II}, Co^{II} and Cu^{II})

The moderate solubility of the ligand in water gave us an opportunity to explore the reactions of this ligand with metal salts in aqueous medium. A mixture of NacNacSO₃Li·2THF and NiCl₂·6H₂O was dissolved in water and stirred for 12 h to afford an off-white precipitate (Scheme 2). Single crystal X-ray diffraction studies



Scheme 1. Synthesis of NacNacSO₃Li·2THF.



Scheme 2. Reaction of $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ with metal chlorides in aqueous medium.

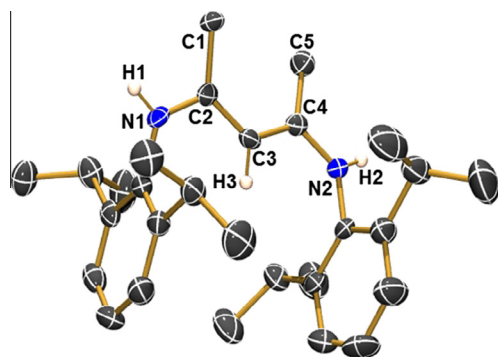
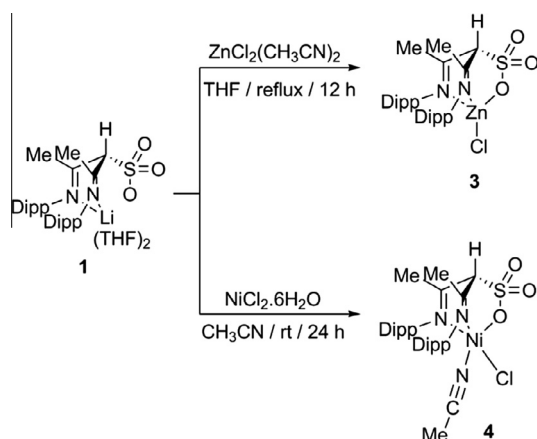


Fig. 2. Crystal structure of $[\text{CH}(\text{C}(\text{Me})=\text{NH}(\text{Dipp}))_2][\text{HSO}_4]$ (**2**). Hydrogen atoms, the counter anion $[\text{HSO}_4]^-$ and the solvent molecule THF are omitted for clarity (except on the N atoms and γ -carbon atom). Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): N1–C2 1.328(4), N2–C4 1.333(4), C1–C2 1.500(4), C4–C5 1.496(4), C2–C3 1.395(4). Selected bond angles ($^\circ$): C1–C2–N1 114.8(2), C5–C4–N2 114.6(3), N1–C2–C3 119.8(3), N2–C4–C3 119.9(3), C4–C3–C2 126.8(3).



Scheme 3. Synthesis of Zn and Ni complexes of $[\text{NacNacSO}_3]^-$.

performed on the crystals grown from the precipitate revealed that it was a β -diketiminium bisulfate salt $[\text{CH}(\text{C}(\text{Me})=\text{NH}(\text{Dipp}))_2][\text{HSO}_4]$ (Dipp = 2,6-diisopropylphenyl). The structure was further supported by a ^1H NMR spectrum. An ORTEP diagram, along with important bond lengths and bond angles, is given in Fig. 2. The same product was obtained when $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ was treated with $\text{CuCl}_2\cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ and ZnCl_2 under similar conditions.

3.3. Reactions of $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ with metal chlorides in organic solvents (metal = Zn^{II} , Ni^{II} and Co^{II})

Since the attempts to prepare metal complexes of $[\text{NacNacSO}_3]^-$ in aqueous medium were unsuccessful, the reactions were explored in organic solvents. An equimolar mixture of $\text{NacNacSO}_3\text{Li}\cdot 2\text{THF}$ and $[\text{ZnCl}_2(\text{CH}_3\text{CN})_2]$ in THF under reflux conditions afforded a tripodal

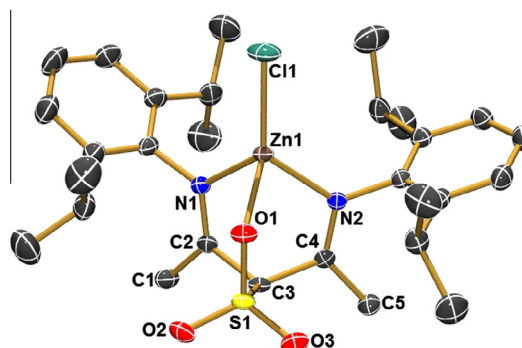


Fig. 3. Crystal structure of $[\text{NacNacSO}_3\text{ZnCl}]$ (**3**). Hydrogen atoms and the solvent molecule toluene are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): C2–N1 1.282(3), C4–N2 1.286(3), C3–S1 1.840(2), S1–O1 1.4865(15), S1–O2 1.4343(15), O1–Zn1 2.0195(14), N1–Zn1 2.0400(17), N2–Zn1 2.0393(17), Zn1–Cl1 2.1485(7). Selected bond angles ($^\circ$): C2–N1–Zn1 115.06(13), C4–N2–Zn1 114.24(13), C3–S1–O1 103.51(9), S1–O1–Zn1 119.68(8), O1–Zn1–Cl1 122.38(4), N1–Zn1–N2 96.18(7), N1–Zn1–Cl1 121.82(5), N2–Zn1–Cl1 125.03(5), N1–Zn1–O1 90.87(6), N2–Zn1–O1 91.82(6).

Zn complex $[\text{NacNacSO}_3\text{ZnCl}]$ (**3**) in good yield (Scheme 3). The formation of the $\text{NacNacSO}_3\text{ZnCl}$ complex was confirmed by single crystal X-ray analysis and NMR spectra. An ORTEP diagram of its molecular structure, important bond lengths and bond angles are given in Fig. 3. $[\text{NacNacSO}_3\text{ZnCl}]$ crystallizes in the $C2/c$ space group of the monoclinic system. The Zn atom adopts a distorted tetrahedral geometry with the ligand coordinating to the metal in an N,N,O chelating fashion, similar to tripodal ligands, and the chloride ion occupies the fourth position. The N1–Zn–N2 bond angle $[96.18(7)^\circ]$ is the smallest of all the bond angles around the Zn centre. The average imine $\text{C}=\text{N}$ distance found in **3** (1.284(3) Å) is typical of $\text{C}=\text{N}$ double bond distance, which indicates the absence of π -delocalization in the backbone of the β -diketimine ligand. The Zn–N and Zn–O bond distances [Zn1–N1 = 2.0400(17), Zn1–N2 = 2.0393(17) and Zn1–O1 = 2.0195(14) Å] are similar to those found in tris(pyrazolyl)methane sulfonate zinc complexes [Zn–N = 2.0484(2)–2.152(2) and Zn–O = 2.017(2)–2.0858(18) Å] [37,38].

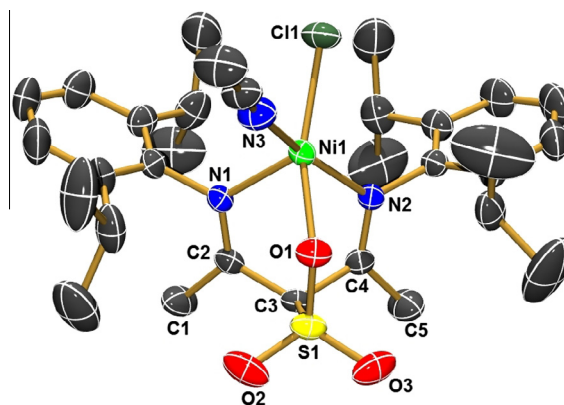


Fig. 4. Crystal structure of $[\text{NacNacSO}_3\text{NiCl}(\text{CH}_3\text{CN})]$ (**4**). Hydrogen atoms and the solvent molecule acetonitrile are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): C2–N1 1.276(2), C4–N2 1.277(2), C3–S1 1.8236(18), S1–O1 1.4683(14), S1–O2 1.4322(16), O1–Ni1 2.0744(13), N1–Ni1 2.0447(15), N2–Ni1 2.0960(14), Ni1–Cl1 2.2539(5), N3–Ni1 2.053(18). Selected bond angles ($^\circ$): C2–N1–Ni1 117.46(13), C4–N2–Ni1 117.00(12), C3–S1–O1 103.31(8), S1–O1–Ni1 122.56(8), N2–Ni1–N3 161.59(7), O1–Ni1–Cl1 158.56(4), N1–Ni1–N2 91.61(6), N1–Ni1–Cl1 111.98(5), N2–Ni1–Cl1 93.77(4), N1–Ni1–O1 89.36(6), N2–Ni1–O1 87.41(6).

Unlike $[\text{ZnCl}_2(\text{CH}_3\text{CN})_2]$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ upon treatment with $\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot 2\text{THF}$ in THF produced a white crystalline material which was found to be insoluble in common organic solvents. Due to its insoluble nature, further characterization could not be carried out. This product is presumed to be a coordination polymer. Nonetheless, when the reaction was carried out in acetonitrile, a green coloured penta-coordinated Ni complex was obtained in moderate yield (Scheme 3). The single crystal X-ray structure of complex **4** (Fig. 4) reveals that the Ni center adopts a distorted square-pyramidal geometry [$\tau = (161.59\text{--}158.56)/60 = 0.05$] [39]. The base of the square-pyramid contains one chloride ion, one nitrogen atom from acetonitrile, one nitrogen atom and one oxygen atom from the ligand. The base is almost planar and the Ni atom lies slightly above (0.349 Å) the mean plane. The apex is occupied by another nitrogen atom from the ligand. Since the ligand coordinates to the metal in a tripodal fashion, the apex is tilted towards the ligand. Important bond lengths and bond angles are listed in Fig. 4. The average imine $\text{C}=\text{N}$ distance found in **4** (1.277(2) Å) is typical of a $\text{C}=\text{N}$ double bond distance. The Ni–N and Ni–O bond distances [Ni1–N1 = 2.0447(15), Ni1–N2 = 2.0960(14) and Ni1–O1 = 2.0744(13) Å] are found to be in the range of those reported for a tris(pyrazoyl)methane sulfonate nickel complex [Ni–N = 2.0964(17) and Ni–O = 2.0438(14) Å] [37,38]. When this green coloured Ni complex was dried under high vacuum, a yellow coloured material was produced, which showed no $\text{C}\equiv\text{N}$ stretching frequency in its IR spectrum. This observation indicates that the acetonitrile is loosely held to Ni. This was further confirmed by elemental analysis. Treatment of $\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot 2\text{THF}$ with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile, afforded a blue coloured Co complex in moderate yield. Attempts to grow the X-ray quality crystals were unsuccessful. The IR spectrum of the complex is similar to that of the Ni complex and further characterization is under progress.

3.4. Reactivity of $\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot 2\text{THF}$ with palladium(II) chloride

When $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ was treated with $\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot 2\text{THF}$ in dichloromethane at room temperature for 18 h, an orange coloured precipitate was formed. This was later characterized as $[\text{CH}(\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2)]_2[\text{SO}_3\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot 2\text{THF}]_2$ (Scheme 4). The crystals, obtained from a mixed acetone and dichloromethane solution of this solid, were subjected to single crystal X-ray diffraction studies. The crystal structure shows a dinuclear anionic complex with a diketiminium ion as the counter cation. To the best of our knowledge, there are only two more examples containing a Pd_2Cl_4 unit with $\text{NaCN} \cdot \text{SO}_3\text{Li}$ based ligands reported in the literature [40,41]. An ORTEP diagram showing the complex anion is given in Fig. 5. Both the Pd centers have a square-planar geometry with two chloride ions bridging the metals. These planes are not coplanar and the dihedral angle between them is 33.25° . This is relatively high compared to that of the reported complexes [19.06° and 5.39°] [40,41]. The central carbon atom of the diketimine ligand is essentially sp^3

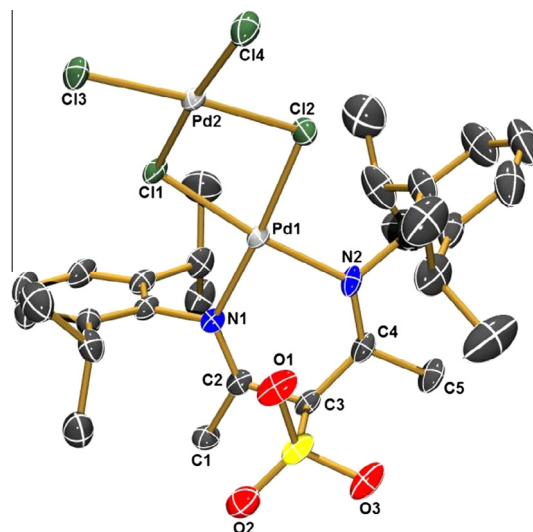
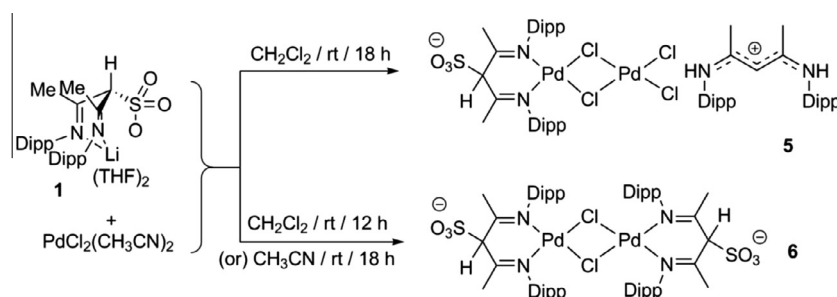


Fig. 5. Crystal structure of $[\text{SO}_3\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot 2\text{THF}]_2[\text{CH}(\text{C}(\text{Me})=\text{NHDipp})_2]_2$ (**5**). Hydrogen atoms, the counter cation $[\text{CH}(\text{C}(\text{Me})=\text{NHDipp})_2]^+$ and three solvent molecules of dichloromethane are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): C2–N1 1.295(7), C4–N2 1.298(7), C3–S1 1.856(5), S1–O1 1.454(4), S1–O2 1.428(5), N1–Pd1 2.017(4), Pd1–Cl1 2.3323(13), Cl1–Pd2 2.3057(13), Pd2–Cl3 2.2742(13). Selected bond angles ($^\circ$): C2–N1–Pd1 126.0(4), C4–N2–Pd1 125.7(4), C2–C3–S1 108.3(3), C3–S1–O1 104.0(2), C3–S1–O2 103.9(3), N1–Pd1–Cl1 93.36(12), N1–Pd2–N2 91.85(17), Pd1–Cl1–Pd2 92.03(4), Cl1–Pd2–Cl2 83.26(5), Cl3–Pd2–Cl4 92.97(5).

hybridized with one hydrogen atom and an $-\text{SO}_3^-$ group attached to it. The $-\text{SO}_3^-$ group is almost perpendicular to the square plane of the Pd atom that is attached to the ligand. It is not involved in coordination with Pd. The Pd–N and Pd–Cl bond distances [Pd1–N1 = 2.017(4) and Pd1–Cl1 = 2.333(13) Å] and N1–Pd1–N2 bond angle [$91.85(17)^\circ$] are similar to those reported for a similar Pd(II) complex [Pd–N1 = 2.013(3), Pd–Cl1 = 2.323(1) Å and N1–Pd–N2 = $89.85(15)^\circ$] [41]. The complex is insoluble in common deuterated solvents, such as chloroform- d , and is sparingly soluble in acetone- d_6 and methanol- d_4 . Because of its poor solubility, a ^{13}C NMR spectrum could not be obtained.

Interestingly, when the reaction was carried out only for 12 h, a yellow coloured compound was produced. Diffraction quality crystals could not be obtained for this complex. The ^1H NMR spectrum of this compound looks essentially the same as that of the anionic portion of the dinuclear Pd complex **5**. No resonances for a counter cation, as in **5**, were observed. The $\nu(\text{S}=\text{O})$ and $\nu(\text{C}=\text{S})$ stretching frequency bands, which appear at 1033 and 627 cm^{-1} , respectively, in the IR spectrum confirm the presence of free $-\text{SO}_3^-$, as in **5**. These bands appear at 1034 and 627 cm^{-1} in the IR spectrum of **5**. Based on these facts and the elemental analysis, this yellow solid was characterized as $[\text{SO}_3\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot \mu\text{-Cl}]_2$ (**6**), in which the Pd centers are bridged by two Cl^- ions. The yield was only 36%.



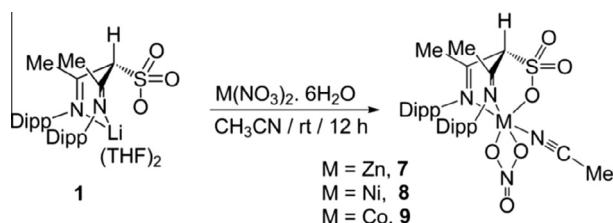
Scheme 4. Reactivity of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with $\text{NaCN} \cdot \text{SO}_3\text{Li} \cdot 2\text{THF}$.

However, when the reaction was carried out in acetonitrile, a good yield (61%) of **6** was achieved. Interestingly, even after 18 h of stirring in acetonitrile, only the formation of **6** was observed. There were no traces of **5**. Our efforts to obtain single crystals from solutions of **6** in acetone, methanol or tetrahydrofuran always yielded a white precipitate, which was found (by NMR) to be the β -diketiminium bisulfate salt $[\text{CH}(\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2)][\text{HSO}_4]$. From these observations, it can be concluded that in the reactions of $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ with $\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Li}\cdot 2\text{THF}$ in dichloromethane or acetonitrile, formation of complex **6** occurs, which decomposes to **5** in dichloromethane on standing.

3.5. Reactions of $\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Li}\cdot 2\text{THF}$ with metal nitrates (metal = Zn^{II} , Ni^{II} and Co^{II})

We further explored the coordination behavior of the tripodal ligand $\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Li}\cdot 2\text{THF}$ with metal nitrates. All the reactions of **1** with metal nitrates were carried out in acetonitrile. Stirring an equimolar mixture of **1** and $\text{M}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Zn}$, Ni and Co) at room temperature afforded a quantitative yield of the corresponding metal complex with the general formula $[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{M}(\text{O}_2\text{NO})(\text{CH}_3\text{CN})]$ ($\text{M} = \text{Zn} = \textbf{7}$, $\text{M} = \text{Ni} = \textbf{8}$, $\text{M} = \text{Co} = \textbf{9}$) (Scheme 5).

All the complexes were characterized by single crystal X-ray analyses and the ORTEP diagrams of the molecular structures are given in Figs. 6–8. The crystal structures reveal that the metal centers adopt a distorted octahedral geometry. The ligand, which coordinates in a tripodal fashion, occupies a face of the octahedron. The remaining corners are occupied by the nitrate ion and one acetonitrile molecule. It is noticed that the coordinated acetonitrile molecule exhibits a positional variation. In the Zn and Co complexes it occupies a position *trans* to one of the imino groups, whereas in the Ni complex, it coordinates to the metal from a position *trans* to the sulfonate group.



Scheme 5. Syntheses of Zn, Ni and Co nitrate complexes.

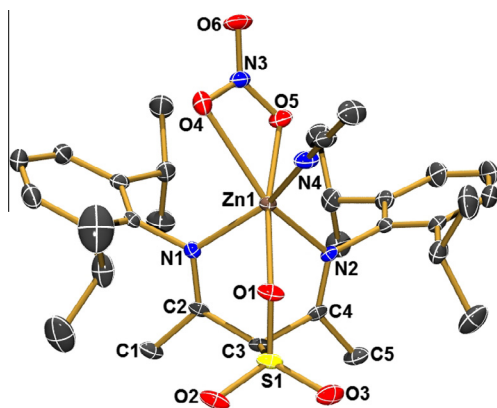


Fig. 6. Crystal structure of $[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Zn}(\text{O}_2\text{NO})(\text{CH}_3\text{CN})$ (**7**). Hydrogen atoms and the solvent molecule acetonitrile are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

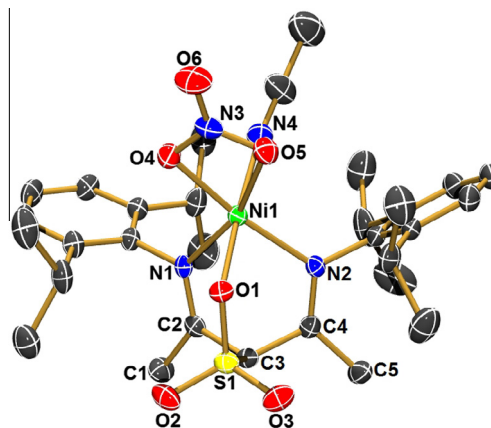


Fig. 7. Crystal structure of $[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Ni}(\text{O}_2\text{NO})(\text{CH}_3\text{CN})$ (**8**). Hydrogen atoms and the solvent molecule acetonitrile are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

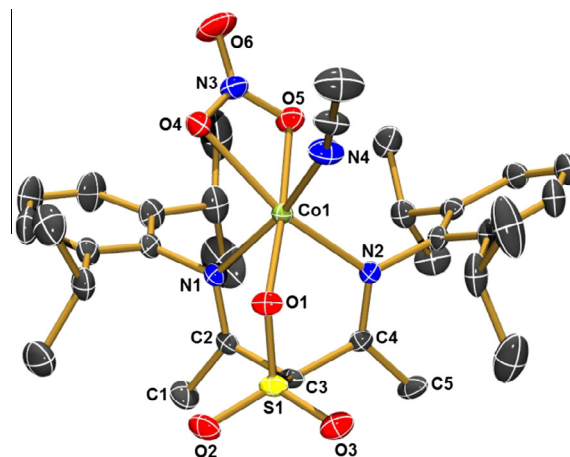


Fig. 8. Crystal structure of $[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Co}(\text{O}_2\text{NO})(\text{CH}_3\text{CN})$ (**9**). Hydrogen atoms and the solvent molecule acetonitrile are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

The dihedral angles between the three planes of the tripodal structure are listed in Table 2. The angles, which are expected to be 120° for an ideal tripodal chelation, deviate significantly due to the difference in the steric crowding on the coordinating atoms. The dihedral angle between the planes passing through the imine groups is significantly higher than the other two angles due to the presence of large isopropyl groups on the imine N atoms, and also due to the absence of a substituent on the sulfonate O atom.

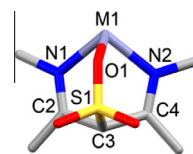


Table 2
A comparison of the torsion angles.

Complex	Z ($^\circ$)	X ($^\circ$)	Y ($^\circ$)
$[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{ZnCl}]$	114.57	114.59	130.84
$[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{NiCl}(\text{CH}_3\text{CN})]$	116.84	114.24	128.92
$[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Zn}(\text{O}_2\text{NO})(\text{CH}_3\text{CN})]$	113.34	114.90	131.76
$[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Ni}(\text{O}_2\text{NO})(\text{CH}_3\text{CN})]$	115.01	115.71	129.28
$[\text{Na}[\text{C}(\text{Me})=\text{NH}(\text{Dipp})_2]\text{SO}_3\text{Co}(\text{O}_2\text{NO})(\text{CH}_3\text{CN})]$	114.32	117.28	128.40

Table 3

Selected bond lengths and bond angles for the Zn, Ni and Co nitrate complexes.

	[NacNacSO ₃ Zn (O ₂ NO)(CH ₃ CN)]	[NacNacSO ₃ Ni (O ₂ NO)(CH ₃ CN)]	[NacNacSO ₃ Co (O ₂ NO)(CH ₃ CN)]
<i>Bond distances (Å)</i>			
C2–N1	1.281(2)	1.283(3)	1.276(2)
C4–N2	1.278(2)	1.275(3)	1.284(3)
C3–S1	1.8249(18)	1.824(2)	1.8268(17)
S1–O1	1.4709(14)	1.4740(17)	1.4763(12)
S1–O2	1.4422(14)	1.4444(19)	1.4398(13)
O1–M1	2.1975(13)	2.0760(16)	2.0861(11)
M1–O4	2.4580(15)	2.0888(17)	2.2028(13)
M1–O5	2.0785(14)	2.1423(18)	2.0812(12)
O4–N3	1.261(2)	1.281(3)	1.257(2)
O5–N3	1.285(2)	1.271(3)	1.287(2)
N3–O6	1.217(2)	1.218(3)	1.212(2)
M1–N4	2.0510(17)	2.069(2)	2.0946(16)
M1–N1	2.0810(15)	2.062(2)	2.1528(13)
<i>Bond angles (°)</i>			
C2–N1–M1	117.61(13)	117.5(16)	117.08(11)
C4–N2–M1	117.74(13)	117.86(17)	117.94(11)
C3–S1–O1	103.73(8)	103.92(10)	104.32(7)
C3–S1–O2	105.33(8)	104.70(11)	104.35(8)
O1–M1–O4	126.78(5)	89.82(7)	113.67(5)
O1–M1–O5	169.21(5)	87.67(7)	172.90(5)
O4–N3–O5	116.46(15)	115.37(19)	115.28(14)
N1–M1–O4	87.98(5)	99.67(7)	88.12(5)
N2–M1–O5	91.05(5)	107.23(7)	98.21(5)
N1–M1–N2	92.20(6)	91.68(8)	90.04(5)
O4–N3–O6	122.56(17)	121.9(2)	123.06(17)
O1–M1–N1	85.02(5)	88.22(7)	86.60(5)
O1–M1–N2	87.27(5)	88.55(7)	88.21(5)

Selected bond angles and distances are listed in Table 3. The N1–M–N2 bond angle around the metal center in the three complexes vary slightly (Zn = 92.20(6)°, Ni = 91.68(8)° and Co = 90.04(5)°). All the three complexes exhibit similar M1–N1, M1–N2 and M1–O1 bond distances (Table 3). The M–O1 bond distances [Zn1–O1 2.1975(13), Ni1–O1 2.0760(16) and Co1–O1 2.0861(11) Å] are found to be in the same range as for tris(pyrazoyl)methane sulfonate metal complexes [Zn1–O1 2.0858(18)–2.017(2), Ni1–O1 2.0438(14) and Co1–O1 2.0861(11) Å] [37,38].

The average imine C=N bond distance found in the three complexes (av. 1.2795 Å) is in the range for a typical C=N double bond. Surprisingly, there are no structural reports in the CCDC on transition metal nitrate complexes of β -diketimine or its anion. The NMR spectra recorded for vacuum dried crystals of **7** did not show an acetonitrile peak. The absence of a stretching frequency band for C≡N ($\nu \sim 2200 \text{ cm}^{-1}$) in the IR spectra, in all cases, indicates that acetonitrile can easily be removed from these complexes by applying a vacuum.

3.6. IR data for all SO₃ substituted compounds

The $\nu(\text{S–O})$ and $\nu(\text{C–S})$ stretching frequencies in the IR spectra of the ligand [NacNacSO₃Li·2THF] and all its metal complexes are listed in Table 4. It is noteworthy that the $\nu(\text{S–O})$ stretching frequency is lower in all the cases where the –SO_3^- group is involved

Table 4The IR stretching frequencies for SO₃[−] substituted compounds.

Compound	$\nu(\text{S–O}) \text{ cm}^{-1}$	$\nu(\text{C–S}) \text{ cm}^{-1}$
NacNacSO ₃ Li·2THF	1050 (vs)	628 (m)
[NacNacSO ₃ ZnCl]	1022 (m)	661 (m)
[NacNacSO ₃ NiCl]	1013 (m)	662 (m)
[NacNacSO ₃ Zn(O ₂ NO)]	1008 (s)	661 (s)
[NacNacSO ₃ Ni(O ₂ NO)]	1017 (vs)	661 (s)
[NacNacSO ₃ Co(O ₂ NO)]	1016 (s)	660 (s)
[SO ₃ NacNacPd ₂ Cl ₄]	1034 (s)	630 (s)
[SO ₃ NacNacPdCl ₂] ₂	1033 (m)	627 (m)

in coordination. In the case of the Pd complexes the $\nu(\text{S–O})$ stretching frequency is higher than the other transition metal complexes, but lower than the ligand. A reverse trend was observed in case of the $\nu(\text{C–S})$ stretching frequency. All the complexes in which –SO_3^- coordinates to the metal show higher $\nu(\text{C–S})$ stretching frequencies.

4. Conclusion

The water soluble tripodal NacNacSO₃Li·2THF ligand has been synthesized. However, it could not be used in aqueous medium because of the ready cleavage of its sulfonate group. When the ligand was treated with divalent chlorides of Ni, Co, Cu and Zn in aqueous medium, the –SO_3^- group was cleaved and produced the β -diketimine salt [CH(C(Me)=NHDipp)₂][HSO₄]. Nonetheless, reactions carried out in organic solvents produced the complexes [NacNacSO₃Zn(Cl)] and [NacNacSO₃Ni(Cl)(CH₃CN)], in which the NacNacSO₃[−] ligand shows a typical tripodal coordination mode. An interesting observation was made in the reaction of the ligand with [PdCl₂(CH₃CN)₂] in dichloromethane. When the reaction was carried out for 18 h, a μ -Cl bridged, boat shaped complex with a Pd₂Cl₄ core was formed, whereas, when the reaction was stopped after 12 h of stirring, a μ -Cl bridged Pd₂Cl₂ complex was obtained. The NacNacSO₃Li ligand formed the distorted octahedral complexes [NacNacSO₃Zn(O₂NO)(CH₃CN)], [NacNacSO₃Ni(O₂NO)(CH₃CN)] and [NacNacSO₃Co(O₂NO)(CH₃CN)] when it was treated with divalent metal nitrates in acetonitrile. Most of the complexes were characterized by single crystal X-ray diffraction studies.

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Appendix A. Supplementary data

CCDC 966290–966296 contain the supplementary crystallographic data for compounds **2–5** and **7–9** respectively. These data can be obtained free of charge via <http://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 e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2014.01.021>.

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