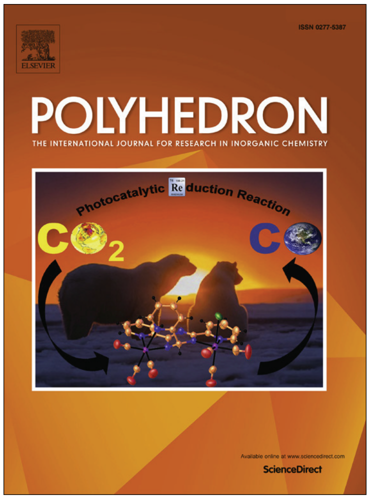


Synthesis and Characterization of First Row Transition Metal *p*-Toluenesulfonate Complexes and Chains

Philp J. Ferko, Jeffrey R. Withers, Hung Nguyen, Charles Allison, Joshua Ema, Tim Ema, Nigam P. Rath, Yuan-Zhu Zhang, Stephen M. Holmes

PII: S0277-5387(16)30646-5
DOI: http://dx.doi.org/10.1016/j.poly.2016.11.047
Reference: POLY 12355

To appear in: *Polyhedron*

Received Date: 30 August 2016
Revised Date: 17 November 2016
Accepted Date: 30 November 2016

Please cite this article as: P.J. Ferko, J.R. Withers, H. Nguyen, C. Allison, J. Ema, T. Ema, N.P. Rath, Y-Z. Zhang, S.M. Holmes, Synthesis and Characterization of First Row Transition Metal *p*-Toluenesulfonate Complexes and Chains, *Polyhedron* (2016), doi: http://dx.doi.org/10.1016/j.poly.2016.11.047

Synthesis and Characterization of First Row Transition Metal *p*-Toluenesulfonate Complexes and Chains

Philp J. Ferko[a], Jeffrey R. Withers[a], Hung Nguyen[a], Charles Allison,[a] Joshua Ema[c], Tim Ema[d], Nigam P. Rath[a,b], Yuan-Zhu Zhang[a], and Stephen M. Holmes[a,b]*

[a] *Department of Chemistry and Biochemistry, University of Missouri-St. Louis, St. Louis, MO 63121, USA*
[b] *Center for Nanoscience, University of Missouri-St. Louis, St. Louis, MO 63121, USA*
[c] *Lutheran High School, South, St. Louis, MO 63123, USA*
[d] *McCluer Senior High School, Florissant, MO 63031, USA*

Abstract

The preparation, structures, and spectroscopic properties of several molecular complexes and a one dimensional chain are described. One-dimensional $\{trans\text{-}Cr^{II}(DMF)_2(OTs)_2\}_n$ (**1**) chain and mononuclear complexes of $trans\text{-}[M^{II}(OTs)_2(DMF)_4]$ (M^{II} = Fe, **2**; Co, **3**) and $[Ni^{II}(DMF)_6][OTs]_2$ (**4**) stoichiometry are readily obtained from DMF/Et_2O solutions containing the parent anhydrous tosylate salts. A hydrated analogue, $trans\text{-}[Fe^{II}(OTs)_2(OH_2)_2(DMF)_2]$ (**5**), is obtained in minor quantities from solutions containing **2**. Electronic spectra indicate all of the complexes adopt octahedral geometries in dimethylformamide solution. Room temperature susceptibility data indicates that high spin electronic configurations are preferred for **1** ($S = 2$), **2** ($S = 2$), and **3** ($S = {}^3/_2$) while **4** adopts an $S = 1$ spin ground state. The solubility properties of the salts are also described.

Keywords: Cyanometalates; Crystal Structures; Magnetic Properties; Single-Molecule Magnets; Polynuclear Complexes

1. Introduction

Binary complexes containing weakly-coordinating anions [1-9] are useful reagents for elaboration into more complex starting materials under a range of synthetic conditions [10-13]. Among these are the venerable perchlorate salts which are known for many alkali/alkaline earth [14-30], main group [14,15,31-36], early [14,15,17,26,33,37-54] and late [14,15,26,33,55-62] transition metal, and several lanthanide and actinide cations [14,15,54,63-66]. Unfortunately these highly soluble salts [14,15,49-51,67-72] all are potentially explosive in the presence of organic ligands and solvents [7,14,15,40,69]. Consequently there has been continuing interest in developing synthetic methods that exploit other weakly-coordinating and non-oxidizing counteranions such as tetrafluoroborate [1,7,8,49-51,72-79], hexafluorophosphate [7,8,49-51], hexafluorosilicate [1,80-85], and tetra(aryl)borates [1,9,86-90] to eliminate the inherent dangers associated with perchlorate use. However, while these anions are not considered as oxidants both BF_4^- and PF_6^- have a propensity to undergo hydrolysis in aqueous media and generate corrosive HF solutions [1-9,91]. In contrast, tetra(aryl)borates can coordinate metal ions via π bonding, are light-sensitive, and contain cleavable B-C bonds [1,86-89].

Despite their redox and hydrolytic stability the well-known sulfates [16,92-106] and Tutton's [16,100-122] salts are unsuitable for many transformations owing to their insolubility in most organic solvents [16,40,103]. In an effort to increase their general utility chemists naturally sought to modify the solubility of the dianionic sulfates via insertion of functional groups to afford monoanionic sulfonate derivatives. Examples include halo- [1,4,123-128], methane- [1,4-6,129-135], trifluoromethyl- [1,4-6,134-165], and various arylsulfonate [1,4-6,122,132,133,161-182] analogues. The higher solubility and rapid substitution kinetics are often exploited to afford clean reaction products and higher chemical yields [1,4,169,183-190].

There has been increasing interest in the use of binary transition metal trifluoromethanesulfonates ("triflates") and *p*-toluenesulfonates ("tosylates") as starting materials in inorganic syntheses owing to their high redox and hydrolytic stability under a range of chemical conditions [1,3-6,10-13,183-189]. The preparations of both salts generally involve: (1) acid addition to metal carbonates, hydroxides, or carboxylates or (2) treatment of metal halides with silver salts [4,135]. General procedures for their preparations from metal powders and aqueous acids were also recently reported [5,6]. Although the synthetic utility of triflates are well appreciated the corresponding tosylate analogues receive comparatively less attention in the chemical literature which may be related to their lower solubility than the corresponding triflates [4-6,171,174,178,186,190].

Hydrated tosylate salts are inexpensive to prepare, can be isolated in high crystalline yields, and are soluble in many polar solvents (e.g. methanol, water, and dimethylformamide) [5,6,171,175,184,187]. In an effort to increase their solubilities in a range of solvents we sought to replace coordinated aqua ligands for those that do not engage in intermolecular hydrogen bonding interactions. We reasoned that substitution for dimethylformamide (DMF) would encourage the formation of anhydrous molecular complexes with higher solubilities than the hydrates [156,185-187].

Structural reports describing sulfate and sulfonate derivatives are commonplace in the chemical literature. Among these are the Tutton [16,100-121], halosulfonates [123-128], methane- [129-136], and arylsulfonate salts [133,135,166-183]. These generally adopt very complicated structures owing to extensive hydrogen bonding interactions between anions and water molecules present. In comparison the structures of binary transition metal *p*-toluenesulfonates are less explored and have been described for relatively few alkali [173,174], transition [122,133-135,175-180,182,183,185-187], and lanthanide metal derivatives [169]. In an effort to better understand the coordination chemistry of tosylate anions and how donor ligands act to influence crystal packing in the solid state we chose to investigate a series of DMF solvates. We now describe the syntheses and X-ray structures of three mononuclear complexes and a one dimensional *p*-toluenesulfonate chain.

2. Experimental

2.1. General Considerations

All operations were conducted under an argon atmosphere using standard Schlenk and drybox techniques. Solution transfers utilized stainless steel cannulas. The preparation of anhydrous tosylate salts were previously described [5,6]. Solvents were distilled under dinitrogen from Na/benzophenone (diethyl ether) or dried over activated alumina (*N*,*N*´-dimethylformamide, DMF) and sparged with argon prior to use. Elemental analyses were performed by Robertson Microlit Laboratories.

2.2. Preparation of Complexes

*2.2.1 Synthesis of {trans-$Cr^{II}(OTs)_2(DMF)_2\}_n \cdot nH_2O$ (**1**)*

Solid $Cr(OTs)_2$ (2.00 g, 5.07 mmol) was dissolved in DMF (10 mL) with stirring and the pale blue-green solution was layered with Et_2O (30 mL). After 7 days the pale blue crystals were isolated via suction filtration, washed with Et_2O (2 × 5 mL), and dried under vacuum for 2 min. at room temperature. Yield: 1.68 g (59.4%). Anal. Calcd for $C_{20}H_{30}N_2O_9S_2Cr$ (**1**): C, 43.00; H, 5.42; N, 5.01. Found: C, 42.67; H, 5.22; N, 4.67. IR (Nujol, cm^{-1}): 3304 (w), 3148 (w), 1919 (w), 1655 (vs), 1497 (s), 1419 (s), 1240 (vs), 1164 (vs), 1120 (vs), 1039 (vs), 1015 (vs), 950 (m), 819 (vs), 801 (s), 703 (vs), 685 (vs), 588 (s), 559 (vs), 420 (m). UV-vis (DMF): λ_{max}/nm (ε_M/M^{-1} cm^{-1}) 725 nm (19). μ_{eff} (μ_B) = 5.02

*2.2.2 Synthesis of {trans-[$Fe^{II}(OTs)_2(DMF)_4$]}$\cdot H_2O$ (**2**)*

Solid $Fe(OTs)_2$ (2.00 g, 5.02 mmol) was dissolved in DMF (10 mL) with stirring and the pale green solution was layered with Et_2O (30 mL). After 7 days the white crystals were isolated via suction filtration, washed with Et_2O (2 × 5 mL), and dried under vacuum for 2 min. at room temperature. Yield: 1.44 g (40.4%). Anal. Calcd for $C_{26}H_{44}N_4O_{11}S_2Fe$ (**2**): C, 44.06; H, 5.91; N, 7.21. Found: C, 44.07; H, 6.26; N, 7.91. IR (Nujol, cm^{-1}): 3291 (m, br), 3012 (m), 3000 (m), 2951 (vs), 2923 (vs), 2854 (vs), 1693 (m), 1648 (vs, br), 1616 (s, sh), 1600 (m, sh), 1497 (s), 1457 (s), 1440 (s), 1411 (s), 1376 (vs), 1285 (w), 1248 (vs), 1216 (s), 1169 (vs), 1119 (s), 1106 (s), 1097 (s), 1063 (m), 1047 (m), 1011 (vs), 865 (w), 854 (w), 825 (s), 815 (m), 799 (w), 714 (w), 682 (s), 575 (m), 567 (s), 560 (s), 492 (w), 411 (m), 401 (m). $\mu_{eff}(\mu_B)$ = 4.82

*2.2.3 Synthesis of trans-[$Co^{II}(OTs)_2(DMF)_4$] (**3**)*

Solid $Co(OTs)_2$ (2.00 g, 4.98 mmol) was dissolved in DMF (10 mL) with stirring and the pink solution was layered with Et_2O (30 mL). After 7 days the pink/orange crystals were isolated via suction filtration, washed with Et_2O (2 × 5 mL), and dried under vacuum for 2 min. at room temperature. Yield: 1.77 g (51.2%). Anal. Calcd for $C_{26}H_{42}N_4O_{10}S_2Co$: C, 45.02; H, 6.10;

N, 8.08. Found: C, 44.45; H, 5.70; N, 7.74. IR (Nujol, cm^{-1}): 3013 (m), 3001 (s), 2952 (vs), 2923 (vs), 2867 (vs), 2854 (vs), 1693 (m), 1648 (vs, br), 1613 (s, sh), 1602 (s), 1497 (s), 1457 (s), 1439 (s), 1416 (s), 1411 (s), 1375 (vs), 1284 (w), 1245 (vs), 1228 (s), 1183 (s), 1169 (vs), 1120 (vs), 1107 (vs), 1096 (vs), 1063 (w), 1039 (s), 1011 (vs), 866 (vs), 854 (vs), 826 (s), 815 (m), 800 (w), 713 (w), 689 (vs), 682 (vs), 576 (s), 656 (vs), 559 (vs), 414 (m), 401 (m). UV-vis (DMF): λ_{max}/nm (ε_M/M^{-1} cm^{-1}) 479 (11), 497 (14), 527 (19). μ_{eff} (μ_B) = 3.87

*2.2.4 Synthesis of [Ni(DMF)$_4$][OTs]$_2$ (**4**)*

Solid Ni(OTs)$_2$ (2.00 g, 4.98 mmol) was dissolved in DMF (10 mL) with stirring and the green solution was layered with Et_2O (30 mL). After 7 days the pale green crystals were isolated via suction filtration, washed with Et_2O (2 × 5 mL), and dried under vacuum for 2 min. at room temperature. Yield: 2.10 g (60.9%). Anal. Calcd for $C_{26}H_{42}N_4O_{10}S_2Ni$ (**4**): C, 45.03; H, 6.10; N, 8.08. Found: C, 44.75; H, 6.06; N, 7.91. IR (Nujol, cm^{-1}): 3143 (m), 3083 (m), 3062 (m), 3048 (m), 3015 (s), 3003 (s), 2955 (vs), 2924 (vs), 2867 (vs), 2855 (vs), 1690 (s, sh), 1653 (vs, br), 1611 (vs, sh), 1601 (s, sh), 1497 (vs), 1455 (vs), 1439 (vs), 1417 (s), 1410 (vs), 1402 (vs), 1372 (vs), 1283 (s), 1244 (vs), 1227 (vs), 1213 (vs), 1170 (vs), 1119 (vs), 1108 (vs), 1098 (vs), 1063 (s), 1048 (s), 1035 (vs), 1012 (vs), 868 (m), 855 (m), 849 (m), 825 (vs), 800 (s), 713 (s), 691 (vs), 681 (vs), 636 (w), 578 (s), 565 (vs), 558 (vs), 498 (w). UV-vis (DMF): λ_{max}/nm (ε_M/M^{-1} cm^{-1}) 402 (11), 679 (4.2), 739 (4.3). μ_{eff}(μ_B) = 2.71

2.3 IR and UV-vis Spectroscopies and Magnetic Measurements

Infrared spectra were recorded as Nujol mulls between KBr plates on a Thermo-Fisher 6700 FTIR instrument in the 400-4000 cm^{-1} region. Electronic spectra were obtained on an Ocean Optics Flame-S-UV-VIS-ES spectrophotometer equipped with a DH-2000-BAL balanced deuterium tungsten source in the 200 to 850 nm range as DMF solutions. Magnetic susceptibility data was collected on a Johnson-Matthey susceptometer using solid Hg[Co(NCS)$_4$] as a reference standard. Diamagnetic corrections were estimated using Pascal's constants [190].

2.4 Structural Determinations and Refinements

X-ray diffraction data for **1** and **3** were collected at 90.0(2) K on a Nonius kappaCCD diffractometer from irregular shaped crystals mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained (DENZO) [191] from ten 1° frames and were refined via a least-squares scheme using all data-collection frames (SCALEPACK) [191]. Lorentz/polarization corrections were applied during data reduction. The structures were solved by direct methods (SHELXS97) [192] and completed by difference Fourier methods (SHELXL97) [192]. Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL97) [192], and empirical absorption corrections (either SCALEPACK [191] or SADABS [193]) were applied.

Single crystal structural data for **2**, **4**, and **5** were collected at 100(2) K on a Bruker Apex-II CCD diffractometer using graphite-collimated MoKα radiation. All crystals were mounted in Paratone-N oil on glass fibers. The structures were solved by direct methods (SHELXS97) [192] and completed by difference Fourier methods (SHELXL97) [192]. Refinement was performed against F^2 by weighted full-matrix least-squares (SHELXL2013) [194] and empirical absorption corrections (SADABS) [193] were applied. The phenyl rings in **5** are disordered and were modelled with two partial occupancy rings at 50% each. The C4-C3´ bond was refined with rigid bond constraint (DELU) while an EADP displacement parameter constraint was used for the C4-C3 one. Hydrogen atoms for **1-5** were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the *International Tables for Crystallography Vol. C. 82* [195]. All figures were generated using CrystalMaker® (CrystalMaker Software Ltd, www.crystalmaker.com).

3. Results and discussion

3.1 Synthesis and spectroscopic characterization

Under an inert atmosphere a series of six-coordinate divalent transition metal salts are easily prepared by aqueous digestion of finely divided metal powders with *p*-toluenesulfonic acid [5,6]. The crystalline hexaaquo salts readily crystalize from aqueous solution and their structures have been previously reported [6,133-138,172,175-180,182,183,185-187]. The salts are easily dehydrated under vacuum [5,6] and may be dissolved in dimethylformamide (DMF)/diethyl ether mixtures to form either a solvated chain, {*trans*-Cr^{II}(OTs)$_2$(DMF)$_2$}$_n$·*n*H$_2$O (**1**) or mononuclear complexes of *trans*-[M^{II}(OTs)$_2$(DMF)$_4$]·*n*H$_2$O (M = Fe, **2**; *n* = 1; Co, **3**; *n* = 0) and [Ni^{II}(DMF)$_4$][OTs]$_2$ (**4**) stoichiometry. Small quantities of *trans*-[Fe^{II}(OTs)$_2$(OH$_2$)$_2$-(DMF)$_2$] (**5**) may also be crystallized in minor quantities from wet DMF/Et_2O mixtures of **2**, but efforts to purposely prepare larger quantities of **5** have consistently met with failure. The complexes are highly soluble in H_2O, dimethylformamide, dimethylacetamide, methanol, and pyridine and lower solubility is found for tetrahydrofuran, ethyl acetate, ethanol, dimethyl sulfoxide, acetonitrile, and acetylacetone (Table 1); **4** displays the highest solubility of the series. Interestingly treatment of **1-4** with nitromethane, acetone, chloroform, and dichloromethane rapidly precipitates fine M(OTs)$_2$ powders suggesting these may initially solubilize and rapidly eliminate coordinated DMF ligands. This behavior confirms that the DMF ligands are substitutionally labile under a variety of conditions [133,172,173,181-187,196,197].

The infrared spectra of **1-4** display strong absorptions consistent with the presence of *p*-toluenesulfonate anions and DMF chromophores. For **1** weak aromatic overtones (1919 and 1922 cm^{-1}) are seen in its spectra while the other analogues do not display these absorptions [5,6,196,198]. Additional high intensity absorptions attributed to lattice water ν_{OH} (ca. 3300 cm^{-1}) and DMF ν_{CO} (ca. 1690 cm^{-1}) and ν_{CN} stretches (ca. 1620 and 1497 cm^{-1}) are also seen. Additional medium and weak intensity ν_{OH} and δ_{HOH} absorptions are also seen near ca. 3300 and 1650 cm^{-1} for **1** and **2**, respectively. These δ_{HOH} scissor modes have similar energies and are comparable to those reported for a variety of [M^{II}(OH$_2$)$_6$][OTs]$_2$·*n*H$_2$O hydrates [5,6,198]. The tosylate antisymmetric $\nu_a(SO_2)$ and symmetric $\nu_s(SO_2)$ stretches are in the ranges seen for hexaaquo complexes and are found at ca. 1170 and between ca. 1119-1130 cm^{-1}, respectively. The tosylate δ_{CS} bands are between 559 and 569 cm^{-1} for **1-4** and are similar to those reported for the [M^{II}(OH$_2$)$_6$][OTs]$_2$ series, and are shifted by ca. 10 cm^{-1} to lower energies relative to anhydrous M^{II}(OTs)$_2$ salts [5,6,198]. Additional aromatic CH bending modes (e.g. out-of-plane CH wag, δ_{CH}) are found between 1040 and 801 cm^{-1} verifying that aromatic tolyl rings are present in **1**-**4**.

Electronic spectra collected as DMF solutions for **1**-**4** generally show absorptions that resemble those of octahedral aqua complexes [43,48,80-82,199-214]. The UV-vis spectrum of **1** shows a single broad absorption that is consistent with the presence of an octahedral high spin Cr^{II}_{HS} (S = 4) complex. The absorption is assigned to the spin-allowed $^5T_{2g} \leftarrow {}^5E_g$ transition (725 nm) while an additional and weaker intensity absorption (428 nm) is ascribed to small solution quantities of Cr^{III} [43,80-83,203,204]. In comparison, the UV-vis spectrum of *trans*-$\{Mn^{II}(DMF)_2(OTs)_2\}_n$ (**6**) does not exhibit a discernable absorption owing to the spin- and Laporte-forbidden nature of optical transitions from the $^6A_1$ ground state [196]. The data indicates that the chains fragment in solution and afford octahedral complexes.

For compound **2** a single spin-allowed $^5E_g \leftarrow {}^5T_{2g}$ electronic transition (ca. 1000 nm) is expected for the Fe^{II}_{HS} cations but the absorption lies outside the energy range investigated. Consistent with this assumption a small shoulder (850 nm) is seen in the optical spectrum of **2** [201,205,206]. Compound **3** displays electronic transitions that are typical of high spin octahedral d^7 complexes [186,199-206]. In six-coordinate Co^{II}_{HS} complexes the $^4A_{2g}$ ground state can participate in three light-induced excitations to afford higher energy quartet states [$^4T_{2g}$, $^4T_{1g}$, $^4T_{1g}$], whose origins arise from lowering the symmetries of the ^4F and ^4P terms, respectively. For high spin d^7 $[Co^{II}_{HS}(OH_2)_6]^{2+}$ ions three optical transitions are expected, $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ (ν_1, 1,235 nm), $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ (ν_2, 625 nm), and $^4T_{1g} \leftarrow {}^4T_{1g}(F)$ (ν_3, 515 nm), where spin-allowed transitions from the $^4T_{1g}(F)$ ground state leads to three spin-allowed transitions to $^4T_{2g}$, $^4A_{2g}$, and $^4P_1(P)$ excited states [200,201,204,206]. The lowest energy one (ν_1) occurs in the near-infrared and lies outside our experimental window (350-850 nm) [200-206]. The ν_3 transition dominates the optical spectrum and lower energy shoulders (479 and 497 nm) are found relative to the aqua complex (515 nm) [16,206]. The shoulder origins are ascribed to either spin-orbit coupling, mixing of spin-forbidden transitions, or the presence of lower symmetry complexes in solution [201]. Likewise the intermediate energy absorption (650 nm) is also found at lower energy than the corresponding aqua complex possibly suggesting that DMF is a better donor ligands than water. Comparing the relative energies of optical transitions in three $[Co^{II}_{HS}L_6]^{2+}$ complexes, where L is an aqua, DMF, or DMSO ligands, we find that absorptions for DMSO solvates (1350, 684, 534 nm) [206] are the lowest in the series, suggesting that DMF is an intermediate strength donor ligand. We note aqueous solutions of **3** and $Co(OTs)_2$ give identical spectra and reports of complexes known to contain $[Co^{II}(OH_2)_6]^{2+}$ cations, confirming that tosylates are easily displaced weakly coordinating anions [5,6,201-205].

Under the assumption **4** contains divalent nickel ions in an octahedral environment the electronic spectra are expected to exhibit three absorptions in the UV-visible (350-850 nm) range [201,203-211]. As is typically found for weak-field ligands the ν_2 and ν_3 transitions lead to a green appearance for many $[Ni^{II}L_6]^{2+}$ complexes in solution. The absorption maxima may be used to estimate both Δ_o and B in the frame of the spectrochemical series considering spin-allowed transitions for d^8 ions. For $[Ni^{II}(OH_2)_6]^{2+}$ there are three electronic transitions: $^3T_{2g} \leftarrow {}^3A_{2g}$ (ν_1, 1026 nm), $^3T_{1g}(^3F)$, $^1E_g \leftarrow {}^3A_{2g}$ (ν_2, 741 nm), and $^3T_{1g}(^3P) \leftarrow {}^3A_{2g}$ (ν_3, 395 nm). The energy difference between the A_{2g} and T_{2g} states gives Δ_o = 1026 nm [199-211] and the unsymmetrical nature of the lowest energy band is generally ascribed as intensity stealing from the $^1E_g \leftarrow {}^3A_{2g}$ transition via configurational interactions with the $^3T_{1g}$(F) level. Unfortunately the lowest energy (ν_1) transition for **4**+2DMF lies outside the experimental window and effectively prevents a direct estimation of Δ_o [198,209]. These absorptions arise from $^3T_{1g}(P)$ and split $^1T_{1g}(F)$ transitions from the $^3A_{2g}$ ground state [201]. Within the experimental range investigated $[Ni^{II}(DMF)_6][ClO_4]_2$ displays absorptions at 400, 691, and 735 nm and resembles data collected for **4** in DMF (402, 679, and 739 nm) suggesting they adopt identical solution structures [206,209,211]. Likewise aqueous solutions of $Ni(OTs)_2$ (393, 659, 721 nm) and $[Ni(OH_2)_6][OTs]_2$ display comparable spectra [402, 679, and 739 nm] confirming that the tosylates are outer-sphere anions. In comparison to other $[Ni^{II}L_6]^{2+}$ complexes, where L is MeOH (1186, 703, 400 nm) and DMSO (1294, 700, 771, and 416 nm), the highest energy optical transitions are seen for the weakest donor ligand [206,209,211,212], indicating that DMF is an intermediate strength donor as expected.

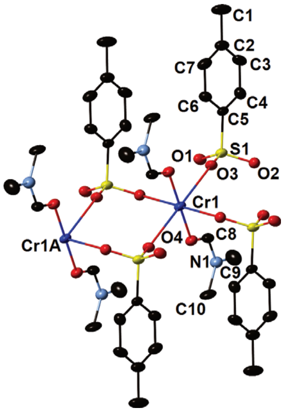


Fig. 1. X-ray structures of one-dimensional chains present approximately along the crystallographic c-direction in **1**-H_2O. Hydrogen atoms are eliminated for clarity and ellipsoids are at the 50% level.

3.2 Crystallographic studies

Compound **1**-H_2O crystallizes as one-dimensional ribbons in the monoclinic $P2_1/n$ space group [Table 2]. The chains bear a structural resemblance to those of $\{trans\text{-}M(L)_2(OTs)_2\}_n$ stoichiometry, reported by Loiseleur and Holmes, respectively, where M = Cd^{2+} and Mn^{II} and L = OH_2 and DMF [6,191,213]. The chains are composed of embedded and corner shared *cis*-$[Cr^{II}_2(\mu\text{-}O_3SC_6H_4Me)_4(DMF)_4]$ squares, where alternate corners are occupied by chromium(II) and tosylate anions [Fig. 1]. The tosylate tolyl rings adopt anti-orientations with respect to the distorted $\{Cr_2S_2\}$ squares and are in close proximity [ca. 5.224(2) Å] to adjacent chains along the crystallographic y-direction, suggesting π-stacking interactions are operative **1** [Fig. 2].

In structures of **1**-H_2O the tolyl rings lie parallel to coordinated DMF ligands and terminal sulfoxide S-O units and bear structural features that are reminiscent of many $[M^{II}(OH_2)_6][OTs]_2$ salts [6,133-138,175-180,182,183,185-187,191,213]. The tosylate bonds in **1**-H_2O and $\{trans\text{-}Mn(DMF)_2(OTs)_2\}_n$ (**6**) are remarkably similar with S1-C [1.773(3) and 1.767(2) Å] and average S1-O bonds [1.457(2) and 1.456(1) Å] seen. Interestingly the $M\text{-}O_{OTs}$ distances in $\{trans\text{-}Mn(DMF)_2(OTs)_2\}_n$ are considerably longer [2.156(1) and 2.194(1) Å] than those in **1**-H_2O suggesting bonding predictions are more complicated than those using only simple electrostatic arguments [Table 3]. We note the Cr1-O distances in **1**-H_2O are longer than those found in tosylate-bridged molecular $\{Cr^{III}_2(\mu\text{-}OTs)_6(THF)_4\}$ squares [1.973(2) Å avg.] being entirely consistent with the presence of divalent chromium centers [215]. The Cr1-O distances in **1**-H_2O range between 2.038(2) and 2.403(2) Å [Cr1-O4 and Cr1-O3] suggesting Jahn-Teller distortions are operative [Table 3]. The elongated axes are oriented parallel to the crystallographic *a*-direction and resemble structures of $[Cr^{II}(OH_2)_6][OTs]$ [2.035(1) and 2.487(1) Å] and $[NH_4]_2[Cr^{II}(OH_2)_6][SO_4]_2$ [2.052(1) to 2.327(1) Å] where Jahn-Teller distortions were also seen [6]. This sharply contrasts those in $[Cr^{II}(OH_2)_6][SiF_6]$, $[Cr^{II}(OH_2)_4][SiF_6]$, and $[Cr^{II}(OH_2)_4][SO_4]{\bullet}H_2O$ [2.106(2), 2.041(1), and 2.053(1) Å], which display little variation in their Cr-O bond lengths [80-82]. However, the latter two salts do have rather long Cr•••F contacts [ca. 2.40(1) Å] reflecting tetragonal elongation associated with Jahn-Teller distortions may indeed be present. The crystallographic data suggests that minimization or elimination of hydrogen bonding interactions in CrO_6 coordination environments may encourage Jahn-Teller distortions to be seen [6,80,82].

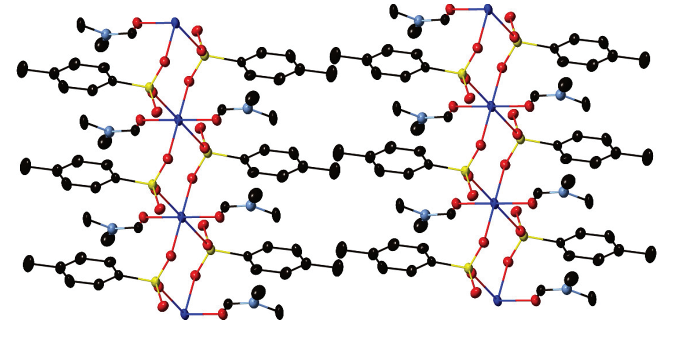


Fig. 2. Packing diagram for **1**-H_2O in the *bc*-plane. Hydrogen atoms are eliminated for clarity and thermal ellipsoids are at the 50% level .

Compounds **2**-H_2O and **3** crystalize as neutral and tetragonally compressed mononuclear complexes in the monoclinic $P2_1/n$ space group [Table 2]. The C_2-symmetric *trans*-$[M^{II}(OTs)_2(DMF)_4]$ complexes contain axial tosylate anions in addition to four coordinated DMF ligands that reside their equatorial planes. The M^{II}-O_{DMF} [2.237(7), Fe1-O1; 2.1574(7) Å, Fe1-O2] bonds in **2**-H_2O are nearly equivalent, while those in **3** [2.231(2), Co1-O1A; 2.049(1) Å, Co1-O1B] are markedly different, suggesting steric crowding or weak Jahn-Teller distortions may be present in the latter. The M^{II}-O_{OTs} [2.0958(7) and 2.028(1) Å] bonds appear to be shorter than the corresponding M^{II}-O_{DMF} ones suggesting significant electrostatic interactions which scale with M^{II} electronegativity are operative in **2**-H_2O and **3**, respectively [Table 3].

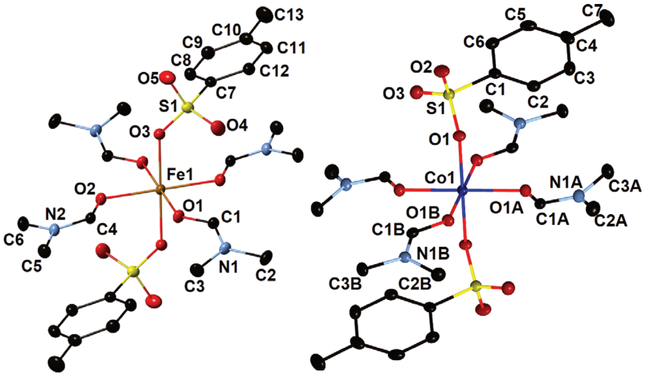


Fig. 3. X-ray structures of (left) **2**-H_2O and (right) **3**. Thermal ellipsoids are at the 50% level and all hydrogen atoms are removed for clarity.

The Fe-O and Co-O bonds in **2**-H_2O and **3** are similar to those found in two dimensional grids of $[M^{II}(BDS)(NMP)_3]$ (M^{II} = Mn, Fe, Co] stoichiometry, where BSD = 1,4-benzenedisulfonate and NMP = *N*-methylpyrrolidone [216]. The structures are composed of two *mer*-$[M^{II}(NMP)_3]^{2+}$ fragments that share common and 4-connected BDS dianion to form cationic one dimensional chains, $\{[M^{II}(NMP)_3]_2(\mu\text{-}1,2\text{-}O_3SC_6H_4SO_3\text{-}\mu\text{-}1,2)\}_n^{2+}$, that propagate along the crystallographic *a*-direction. The chains are linked by additional perpendicular bis(μ-BDS) units along the *b*-direction to give a two dimensional grid of parallel ribbons [216]. The metal coordination spheres have rather long Fe-O_{BDS} [2.1396(5) to 2.1465(5) Å] and Co-O_{BDS} [2.0944(6) to 2.1023(6) Å] distances while the Fe-O_{NMP} and Co-O_{NMP} ones span a larger range [2.0927(5) to 2.1649(5) Å] and [2.0453(6) to 2.1275(6) Å]. In comparison to the Christoffers and Wickleder data the M-O_{DMF} distances are longer in **2**-H_2O [2.237(7) and 2.1574(7) Å] while the Co-O_{DMF} ones in **3** [Table 3] vary considerably [2.231(2) and 2.049(1) Å] [216]. In another structurally characterized chain, $\{trans\text{-}Co(BS)_2(EtOH)_2\}_n$, where BS is a benzenesulfonate anion the Co-O_{BS} [2.132(8) and 2.108(7) Å] and Co-O_{EtOH} bonds [2.049(8) Å] are slightly shorter than the Co-O_{OTs} [2.231(2) and 2.049(1) Å] and Co1-O_{DMF} ones [2.028(1) Å], consistent with ethanol being a weaker donor than DMF as expected. Intramolecular hydrogen bonding interactions between coordinated EtOH and benzenesulfonate ligands are also found and also probably contribute to shorter Co-O distances in their structure [217].

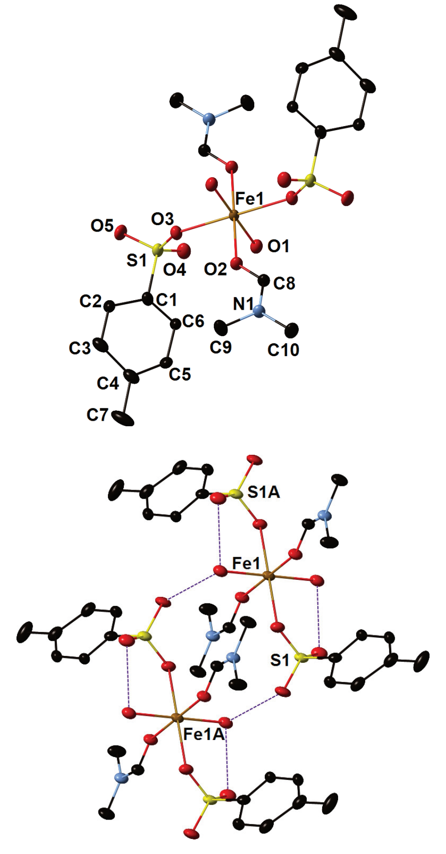


Fig. 4. (top) Molecular structure of **5**. (bottom) X-ray structure of **5** highlighting intra- and intermolecular hydrogen bonding interactions (dotted lines). Hydrogen atoms are eliminated for clarity and ellipsoids are at the 50%

Compounds **2**-H_2O and **3** also bear notable structural similarities to hexaaqua complexes described by Cotton. The M-O bonds in **2** and **3** have average lengths that resemble those observed in $[NH_4]_2[M^{II}(OH_2)_6][SO_4]_2$ Tutton's and $[M^{II}(OH_2)_6]SiF_6$ salts [82]. Interestingly the S1-O3 and S1-O1 distances [1.4793(8) and 1.490(2) Å] are the longest of the sulfonate S-O bonds, suggesting that some charge localization may be operative within the tosylate anions of **2**-H_2O and **3** [Table 3]. Further analysis shows that the O-M^{II}-O angles in **2**-H_2O and **3** deviate significantly from ideal octahedral geometries further indicating steric interactions may lead to structural distortions. The $[M^{II}(OH_2)_6]^{2+}$ cations have O-M^{II}-O angles that range between 89.25(6) and 91.1(1)° (for Fe^{II}) and 88.94(94(3) and 89.69(4)° (for Co^{II}) Tutton's salts, while the hexafluorosilicates are between 88.93(8) and 89.53(4)° [82]. However in both complexes the O-M^{II}-O angles range from slightly acute [88.34(3), O1-Fe1-O2; 83.74(6)º, O1-Co1-O1A] to linear suggesting that steric congestion is more pronounced in the latter complex. This is entirely consistent with the presence of smaller cobalt(II) ions [Table 3].

The molecular tosylates (**2**-H_2O and **5**) may be considered as structural analogues of *trans*-$[Fe(O_3SR)_2(py)_4]$ complexes originally described by Thompson, where R = CF_3, Me, and C_6H_4Me [127,135,176]. The tetragonally compressed *trans*-$[Fe^{II}(OTs)_2(py)_4]$ complexes adopt idealized D_{4h} symmetric FeO_2N_4 coordination environments, where the Fe-N_{py} [2.221(3) and 2.245(3) Å] and Fe-O_{OTs} [2.076(2) Å] bonds are longer and slightly shorter than the corresponding Fe1-O_{DMF} [2.1237(7) and 2.1574(7) Å] and Fe1-O_{OTS} [2.0958(7) Å, Fe1-O3] ones in **2**-H_2O [Table 3]. In structures of **2**-H_2O the M-O_{OTs} bonds are longer than those seen for the entire *trans*-$[Fe^{II}(O_3SR)_2(py)_4]$ series (R = CF_3, Me, C_6H_4Me; 2.11, 2.06, and 2.08 Å] suggesting DMF ligands are slightly better σ donors than pyridine for oxophillic iron centers. Likewise the S-O distances are between 1.421(3) and 1.474(2) Å, with the shortest one corresponding to a terminal sulfoxide unit. In comparison, the S-O bonds in **2**-H_2O range between 1.4466(8) and 1.4793(8) Å, with the coordinated tosylate oxygen [S1-O3] displaying the longest bond of the three.

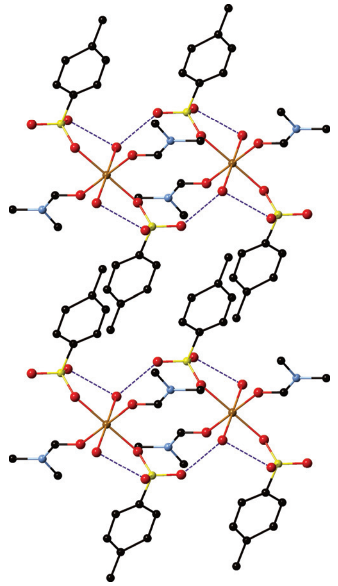


Fig. 5. Packing diagram for **5** viewed along the crystallographic *b*-direction. Intermolecular hydrogen bonding (dotted lines) are found between coordinated aqua and tosylate ligands along the crystallographic *a*-direction. Hydrogen atoms are eliminated, thermal ellipsoids are at the 50% level, and only iron (orange), sulfur (yellow), oxygen (red), nitrogen (blue), and carbon (black) atoms are shown for clarity.

The corresponding Fe-O distances in **5** also display noticeable differences when compared to other iron sulfonate complexes [127,135,140]. Compound **5** crystallizes as a mononuclear complex in the triclinic *P*-1 space group [Table 2 and Fig. 4]. The tosylate bonds are related via rotation and give a C_2-symmetric complex of *trans*-$[Fe^{II}(OTs)_2(OH_2)_4]$ stoichiometry. The tosylate Fe1-O3 bonds [2.1428(8) Å] are between the Fe-O_{aqua} [2.1498(9) Å, Fe1-O1] and Fe-O_{DMF} [2.0804(7) Å] ones in **3** [Table 3] and are similar to the Fe-$O_{sulfate}$ distances seen for *cis*-$[Fe^{II}(\mu\text{-}OSO_3)_2(OH_2)_4]$ units [avg. 2.12(5) Å] in structures of $FeSO_4{\cdot}4H_2O$ [96]. Under the assumption coordinated aqua and DMF ligands are respectable σ donors the Fe-O distances will be dependent on both donor strength and ligand size. Surprisingly, the smaller aqua ligands display rather long Fe-O distances in comparison to the Fe-O_{DMF} ones, suggesting additional effects may be operative (*vide infra*). Upon further inspection both intra- and intermolecular hydrogen bonding contacts [ca. 2.687(3) Å] are present linking coordinated aqua and tosylates along the crystallographic *b*-direction [Fig. 4, right]. We propose these secondary interactions act to decrease aqua ligand basicity and concomitantly elongates their Fe-O_{aqua} bonds. Consistent with this assumption the S1-O3 and S1-C7 bonds [1.4720(9) and 1.767(1) Å] are also comparable to those in **2**, while the remaining S1-O ones are slightly longer, further indicating that hydrogen bonding is important in structures of **5** [Table 3].

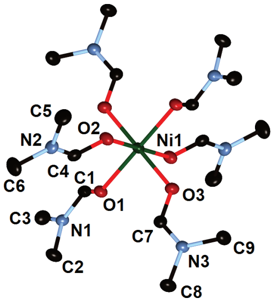


Fig. 6. X-ray structure of the cationic portion of **4**+2DMF. Ellipsoids are at the 50% level and all hydrogen atoms and tosylate anions are removed for clarity.

Complex **4**+2DMF crystallizes as a six coordinate complex in the monoclinic $P2_1/n$ space group [Table 2]. The homoleptic $[Ni^{II}(DMF)_6]^{2+}$ cation has Ni-O bonds that range from 2.042(2) to 2.062(1) Å [Ni1-O3 and Ni1-O2] and are in the typical range seen for six coordinate nickel complexes, being identical to those in $[NH_4]_2Ni^{II}[SO_4]_2{\cdot}6H_2O$ [avg. 2.04(3) Å] [82,106]. The outer sphere tosylate anions exhibit nearly identical S1-O distances [ca. 1.452(2) Å] and slightly longer S1-C bonds in comparison to the other structures supporting the assumption that charge is efficiently delocalized over the SO_3^- fragment [Table 3]. The S-O bonds in **4**+2DMF are only slightly shorter than those seen in Tutton's salt analogues [avg. 1.49(3) Å]. The O-Ni1-O angles range between 89.43(5) and 92.86(5)º and are comparable to those in $[NH_4]_2Ni^{II}[SO_4]_2{\cdot}6H_2O$ [89.5(1) to 92.7(2)°, indicating **4**+2DMF adopts a nearly ideal octahedral coordination geometry [82].

Magnetic measurements confirm the tosylate complexes are paramagnetic and contain divalent transition metal centers. Consistent with previously described spectroscopic data we find orbital contributions are nearly quenched for the octahedral complexes with each adopting effective magnetic moments that are close to the expected spin-only values [190]. The magnetic data indicate that Cr^{II}_{HS} ($S = 2$, 5.02 μ_B), Fe^{II}_{HS} ($S = 2$, 4.82 μ_B), and Co^{II}_{HS} ($S = {}^3/_2$, 3.87 μ_B) and Ni^{II} ($S = 1$, 2.71 μ_B) spin centers are present in **1**-**4**, respectively, where μ_B is the Bohr magneton [190,214]. These data are consistent with charge balance considerations and confirm the validity of previously described spectroscopic and structural data.

4. Conclusions

A series of solvated divalent *p*-toluenesulfonate complexes and chains may be readily prepared and isolated as crystalline materials. The complexes are highly soluble in polar organic media and easily afford desolvated materials in the presence of non- or weakly-coordinating solvents. The spectroscopic properties of dissolved tosylates are similar to mononuclear octahedral aqua complexes indicating that the anions are outer sphere in solution. Magnetic studies confirm the isolated materials contain divalent metal ions with high spin states favoured for the chromium, manganese, iron, and cobalt complexes.

Acknowledgements

S.M.H. gratefully acknowledges the National Science Foundation (CHE-0939987, X-ray upgrade; CHE-1214063) for financial support. High school student training programs Students and Teachers as Research Scientists (STARS; J.E. and T.E.) and American Chemical Society SEED (H.N.) are also thanked for partial support of this research.

Supplementary data

CCDC 1493037 and 1493039-1493041 (**1**-**5**) containing the supplementary crystallographic data may be obtained free of charge via the Internet at 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 (in CIF format) associated with this article can be found in the online version at doi: XXXXXXX.

References

[1] S.H. Strauss, Chem. Rev. 93 (1993) 927;
[2] D.H. Geske, J. Phys. Chem. 63 (1959) 1062;
[3] M.G. Hill, W.M. Lamanna, K.R. Mann, Inorg. Chem. 30 (1991) 4687;
[4] G.A. Lawrance, Chem. Rev. 86 (1986) 17;
[5] S.M. Holmes, S.G. McKinley, G.S. Girolami, Inorg. Synth. 33 (2002) 91;
[6] S.M. Holmes, thesis, Molecule-Based Magnets Constructed from Hexacyanometalates, University of Illinois at Urbana-Champaign, Urbana, 1999;
[7] T.R. Musgrave, T.S. Lin, J. Coord. Chem. 2 (1973) 323;
[8] R.A. Heintz, J.A. Smith, P.S. Szalay, A. Weisgerber, K.R. Dunbar, Inorg. Synth. 33 (2002) 75;
[9] W.E. Buschmann, J.S. Miller, Inorg. Synth. 33 (2002) 83;
[10] N.E. Dixon, G.A. Lawrance, P.A. Lay, A.M. Sargeson, H. Taube, Inorg. Synth. 24 (1986) 342;
[11] J.B. Hendrickson, D.D. Stembach, K.W. Baur, Acc. Chem. Res. 10 (1977) 306;
[12] R.D. Howells, J.D. McCown, Chem. Rev. 71 (1977) 67;
[13] A. Scott, H. Taube, Inorg. Chem. 10 (1971) 62;
[14] R. Roth, Zur Kenntnis der Perchlorate, Munich, 1910, and references cited therein; W.G. Wyckoff, Crystal Structures, 2nd Ed., vol. 3, Interscience, New York, 1960, and references cited therein;
[15] J.C. Schumacher, Perchlorates. Their Properties, Manufacture and Uses. Reinhold Publ. Corp., New York, 1960, and references cited therein;
[16] J.W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, V. 2, Longmans, Green, and Co., London, 1922, and references cited therein;
[17] G.S. Sérullas, Ann Chim. Phys. 46 (1831) 257;
[18] A. Polititzin, J. Russ. Phys. Chem. 19 (1887) 339;
[19] J.W. Retgers, Z. Phys. Chem. 8 (1891) 19;
[20] F. Penney, Liebig's Ann. 37 (1841) 297;
[21] T. Schlössing, Compt. Rend. 73 (1871) 1271;
[22] G.S. Sérullas, Ann Chim. Phys. 46 (1831) 257;
[23] J. von Liebig, Mag. Pharm. 34 (1831) 128;
[24] J.C.G. de Marignac, Bibl. Univ. 45 (1843) 346;
[25] K.G. Roth, Pogg. Ann. 133 (1868) 213;
[26] G.S. Sérullas, Ann Chim. Phys. 46 (1831) 306;
[27] P. Groth, Pogg. Ann. 133 (1868) 226;
[28] A. Atterberg, Ber. 7 (1873) 472;
[29] A. Atterberg, Bull. Soc. Chim. 24 (1875) 358;
[30] J.C.G de Marignac, Ann. Chim. Phys. 46 (1831) 304;
[31] M.M.P. Muir, Chem. News 33 (1876) 15;
[32] G.S. Sérullas, Ann Chim. Phys. 46 (1831) 304;
[33] F.C. Mathers, C.G. Schlüderberg, J. Am. Chem. Soc. 30 (1908) 211;
[34] W. Crookes, Chem. News 8 (1863) pp. 195, 219, 231, 243, 255, 279;
[35] J.W. Retgers, Z. Phys. Chem. 8 (1891) 17;
[36] H.E. Roscoe, Leibig's Ann. 121 (1862) 355;
[37] W. Crookes, Phil. Trans. 15A (1908) 209;
[38] C.D. West, Z. Krist, 91A (1935), 480;
[39] N.V. Sidgwick, The Chemical Elements and Their Compounds, VII, Oxford, 1950;
[40] F. Hein, S. Herzog, Handbook of Preparative Inorganic Chemistry, 2nd Ed., 1965, pp. 1361-1370, Academic, NY;
[41] D.G. Holah, J.P. Fackler, 10 (1967) 26;
[42] F. Sobot, Bull. Soc. Min. 34 (1911) 144;
[43] J. P. Fackler, D.G. Holah, Inorg. Chem. 4 (1965) 954;
[44] S.A. Shchukarev, S.N. Andreev, T.G. Balicheva, L.N. Nechaeva, Ser. Fiz. I Khim. 3 (1961) 120;
[45] G. Monnier, Ann. Chim (Paris) 2 (1957) 14;
[46] C.F. Wells, G. Davies, J. Chem. Soc. A (1967) 1858;
[47] H.E. Roscoe, Liebig's Ann. 121 (1862) 355;
[48] H.L. Schlafer, W. Schaffernicht, Angew. Chem. 72 (1960) 818;
[49] G. Bødtker-Naess, O. Hassel, Norke Videnskaps-Akad. Oslo I. Mat. Naturv. Kl., No. 4 and 7;
[50] G. Bødtker-Naess, O. Hassel, Z. Anorg. Allgem. Chem. 211 (1933) 21;
[51] G. Bødtker-Naess, O. Hassel,Z. Physik. Chem. 22B (1933) 1089;
[52] C.D. West, Z. Krist. 91A (1935) 181;
[53] P. Groth, Pogg. Ann. 133 (1868) 213;
[54] P. Groth, F. Terlikowsky, R. Roth, L´étude de préparation et des propirétés de quelques perchlorates, Geneva, 1911;
[55] P.T. Cleve, Bull. Soc. Chim. 21 (1874) 156;
[56] P.T. Cleve, Bull. Soc. Chim. 23 (1876) 344;
[57] F.P.V. Venable, I.W. Smithey, J. Soc. Chem. Ind. 41 (1919) 1722;
[58] P. Groth, Pogg. Ann. 133 (1868) 226;
[59] H.E. Roscoe, Proc. Roy. Soc. 11 (1862) 502;
[60] H.E. Roscoe, Liebig's Ann. 121 (1862) 356;
[61] G.S. Sérullas, Ann. Chim. Phys. 45 (1831) 2;
[62] H.E. Roscoe, J. Chem. Soc. 19 (1866) 504;
[63] P.T. Cleve, Bull. Soc. Chim. 29 (1878) 492;
[64] S. Jolin, Bull. Soc. Chim. 21 (1874) 533;
[65] G.T. Morgan, E. Cahen, J. Chem. Soc. 91 (1907) 91;
[66] P.T. Cleve Bull. Soc. Chim. 21 (1874) 116;
[67] R. Alexander, E.C.F. Ko, Y.C. Mac, A.J. Parker, J. Am. Chem. Soc. 89 (1967) 3703;
[68] IUPAC Solubility Data Series, 41, Alkaline Earth Metal Perchlorates, Pergamon Press, New York, 1989.
[69] J.C. Schumacher, Perchlorates. Their Properties, Manufacture and Uses., Reinhold Publ. Corp., New York, 1960, and references cited therein;
[70] R. Longhi, R.S. Drago, Inorg. Chem. 4 (1965) 11;
[71] U. Alvisi, Gazz. Chim. Ital. 31 (1901) 289;
[72] O. Hassel, H. Kringstad, Z. Anorg. Allgem. Chem. 209 (1932) 281;
[73] J.J. Habeeb, F.F. Said, D.G. Tuck, J. Chem. Soc., Dalton Trans. (1981) 118;
[74] E. Kamieńska, I. Uruska, Bull. Acad. Pol Sci. Ser. Sci. Chim. 21 (1973) 587;
[75] W.L. Groeneveld, J.J. van Houte, A.P. Zaur, Pecl. Trav. Chim. Pays-Bas, 755 (1968);
[76] D.G.L. Holt, L.F. Larkworthy, D.C. Povey, G.W. Smith, G.J. Leigh, Inorg. Chim. Acta 169 (1990) 201;
[77] R.W. Cockman, B.F. Hoskins, M.J. McCormick, T.A. O'Donnell, Inorg. Chem. 27 (1988) 2742;
[78] N.E. Dixon, G.A. Lawrance, P.A. Lay, A.M. Sargeson, H. Taube, Inorg. Synth. 24 (1986) 259;
[79] E. Kamieńska, I. Uruska, Electrochim. Acta 22 (1977) 181;
[80] F.A. Cotton, L.M. Daniels, C.A. Murillo, Inorg. Chem. 32 (1993) 4868;

[81] F.A. Cotton, L.R. Falvello, C.A. Murillo, J.F. Quesada, J. Solid State Chem. 96 (1992) 192;
[82] F.A. Cotton, L.R. Falvello, C.A. Murillo, J.F. Quesada, Inorg. Chem. 32 (1992) 4861;
[83] O. Hassel, J.R. Salvesen, Z. Physik. Chem. 126 (1927) 345;
[84] W.C. Hamilton, Acta Crystallogr. 15 (1962) 353;
[85] D.J. Sutor, Acta Crystallogr. 12 (1959) 72;
[86] M.B. Hossain, D. van der Helm, Inorg. Chem. 17 (1978) 2893;
[87] R.R. Schrock, J.A. Osborn, Inorg. Chem. 9 (1970) 2339;
[88] M.J. Nolte, G. Gafner, Acta Crystallogr. B30 (1974) 738;
[89] P. Albano, M. Aressa, M. Manassero, Inorg. Chem. 19 (1980) 1069;
[90] S.J. Anderson, F.J. Wells, G. Wilkinson, B. Hussain, M.B. Hursthouse, Polyhedron 7 (1988) 2615;
[91] V.H. Hartmann, H.L.Z. Schlafer, Naturforschg 6A (1951) 754;
[92] A. Earnshaw, L.F. Larkworthy, K.C. Patel, J. Chem. Soc. A (1969) 1339;
[93] M. Géloso, J. Faheme, Nouveau Traité de Chemie Minérale, P. Pascal, Ed., Musson el Cie, VIS (1960) 963;
[94] J.P. Fackler, D.G. Holah, Inorg. Chem. 4 (1965) 954;
[95] W.H. Baur, Acta Crystallogr. 8 (1962) 815;
[96] B.N. Figgis, J. Lewis, Prog. Inorg. Chem. 6 (1964) 37;
[97] C.A. Beevers, H. Lipson, Z. Krist. 82 (1932) 297;
[98] R.B. Corey, R.W.G. Wykoff, Z. Krist. 84 (1933) 477;
[99] C. Frondel, C. Palache, Am. Mineralogist 34 (1949) 188;
[100] D.J. Sutor, Acta Crystallogr. 12 (1959) 72;
[101] J.K. Beattie, S.P. Best, P. Del Favero, B.W. Skelton, A.N. Sobolev, A.H. White, J. Chem. Soc., Dalton Trans. (1996) 1481;
[102] L.F. Larkworthy, J.M. Murphy, K.C. Patel, D.J. Phillips, J. Chem Soc. A (1968) 2936;
[103] A.E.H. Tutton, Phil. Trans. 216 (1916) 1;
[104] R.G.W. Wychoff, Crystal Structures, 2nd. Ed., Interscience, 3 (1965);
[105] N.W. Grimes, H.F. Kay, M.W. Webb, Acta Crystallogr. 16 (1963) 823;
[106] B.N. Figgis, J. Lewis, Prog. Inorg. Chem. 6 (1964) 176;
[107] A. Earnshaw, L.F. Larkworthy, K.C. Patel, G. Beech, J. Chem. Soc. A (1969) 1334;
[108] W.F. Donovan, P.B. Smith, J. Chem. Soc., Dalton Trans. (1975) 894;
[109] K.G. Shields, C.H.L. Kennard, Cryst. Struct. Commun. 1 (1972) 189;
[110] J.J. van der Zee, K.G. Shields, A.J. Graham, C.H.L. Kennard, Cryst. Struct. Commun. 1 (1972) 367;
[111] K.G. Shields, J.J. van der Zee, C.H.L. Kennard, Cryst. Struct. Commun. 1 (1972) 371;
[112] G.H. Brown, R. Chidambaram, Acta Crystallogr. B25 (1969) 676;
[113] R.V. Chastain, J.J. Natt, A.M. Witkowska, E.C. Lingafelter, Acta Crystallogr. 22 (1967) 775;
[114] J.K. Beattie, S.P. Best, P. Del Favero, B.W. Skelton, A.N. Sobolev, A.H. White, J. Chem. Soc., Dalton Trans. (1996) 1481;
[115] L.F. Larkworthy, J.M. Murphy, K.C. Patel, D.J. Phillips, J. Chem Soc. A (1968) 2936;
[116] R.C. Guha, Proc. Roy. Soc. 206A (1951) 353;
[117] T.J. Swift, Inorg. Chem. 3 (1964) 526;
[118] W. Schneider, Acta Crystallogr. 14 (1961) 784;
[119] K. Kohler, W. Frankee, Acta Crystallogr. 17 (1964) 1088;
[120] G. Gattow, J. Zeeman, Z. Anorg. Allgem. Chem. 293 (1958) 23;
[121] N.S. Hush, R.J.M. Hobbs, Prog. Inorg. Chem. 10 (1968) 259;
[122] T.S. Davis, J.P. Fackler, M.J. Weeks, Inorg. Chem. 7 (1968) 1994;
[123] J.N. Brazier, A.A. Woolf, J. Chem. Soc. A (1967) 99;
[124] R.C. Paul, S. Singh, R.C. Kumar, R.D. Sharma, R.D. Verma, Ind. J. Chem. 17A (1979) 273;
[125] R.C. Paul, N.C. Sharma; R.D. Verma, A.K. Sharma, Ind. J. Chem. 14A (1976) 705;
[126] C.S. Alleyne, K. O'Sullivan Mailer, R.C. Thompson, Can. J. Chem. 52 (1974) 336;
[127] J.M. Taylor, R.C. Thompson, Can. J. Chem. 49 (1971) 511;
[128] R.D. Verma, R.C. Kumar, Ind. J. Chem. 15A (1977) 363;
[129] R.C. Paul, V.P. Kapila, S.K. Sharma, Ind. J. Chem. 12 (1974) 651;
[130] R.C. Paul, V.P. Kapila, N. Palta, S.K. Sharma, Ind. J. Chem. 12 (1974) 825;
[131] R. Feld, J. Chem. Soc. (1964) 3963;
[132] R.C. Paul, V.P. Kapila, S.K. Sharma, J. Inorg. Nucl. Chem. 36 (1974) 1933;
[133] S. Kumar, S.K. Gupta, S. K. Sharma, Thermochim. Acta 71 (1983) 193;
[134] A.L. Arduini, M. Garnett, R.C. Thompson, T.C.T. Wong, Can. J. Chem. 53 (1975) 3812;
[135] J.S. Haynes, J.R. Sams, R.C. Thompson, Can. J. Chem. 59 (1981) 669;
[136] D.A. Buckingham, P.J. Cresswell, W.G. Jackson, A.M. Sargeson, Inorg. Chem. 20 (1981) 1647;
[137] W.C. Kupferschmidt, R.B. Jordan, Inorg. Chem. 21 (1982) 2089;
[138] K. Bourmizane, M.H. Herzog-Cance, D.J. Jones, J.L. Pascal, J. Potier, J. Roziere, Polyhedron 10 (1991) 2757;
[139] R.E. Noftle, G.H. Cady, Inorg. Chem. 12 (1966) 2182;
[140] K. Boumizane, M.H. Herzog-Cance, D. Jones, J.L. Pascal, J. Potier, J. Roziere, Polyhedron 10 (1991) 2757;
[141] P.J. Riedel, N. Arulsamy, M.P. Mehn, Inorg. Chem. Commun. 14 (2011) 734;
[142] J.L. Brumaghim, C.L. Gross, G.S. Girolami, J. Organomet. Chem. 691 (2006) 3874;
[143] J.-C. Berthet, M. Nierlich, M. Ephritikhine, Polyhedron 22 (2003) 3475;
[144] J.-C. Berthet, M. Nierlich, M. Ephritikhine, Chimie 5 (2002) 81;
[145] J.-C. Berthet, M. Ephritikhine, Coord. Chem. Rev. 178-180 (1998) 83;
[146] R.J. Batchelor, J.N.R. Ruddick, J.R. Sams, F. Aubke, Inorg. Chem. 16 (1977) 1414;
[147] A. Abbasi, P. Lindqvist-Reis, L. Eriksson, D. Sandström, S. Lidin, I. Persson, M. Sandström, Chem. Eur. J. 11 (2005) 4065;
[148] N.E. Dixon, G.A. Lawrance, P.A. Lay, A.M. Sargeson, H. Taube, Inorg. Synth. 24 (1986) 250;
[149] T. Hayashida, H. Kondo, J.-i. Terasawa, K. Kirchner, Y. Sunada, H. Nagashima, J. Organomet. Chem. 692 (2007) 382;
[150] G.A. Lawrance, A.M. Sargeson, Inorg. Synth. 24 (1986) 263;
[151] P.A. Lay, R.H. Magnuson, J. Sen, H. Taube, J. Am. Chem. Soc. 104 (1982) 7658;
[152] P.A. Lay, Magnuson, R. H.; Taube, H. Inorg. Chem. 1989, 28, 3001-3007.
[153] N.E. Dixon, G.A. Lawrance, P.A. Lay, A.M. Sargeson, H. Taube, Inorg. Synth. 24 (1986) 269;
[154] B. Anderes, S.T. Collins, D.K. Lavallee, Inorg. Chem. 23 (1984) 2201;
[155] N.E. Dixon, W.G. Jackson, M.J. Lancaster, G.A. Lawrance, A.M. Sargeson, Inorg. Chem. 20 (1981) 470;
[156] N.E. Dixon, W.G. Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. Inorg. Synth. 22 (1983) 103;
[157] N.E. Dixon, W.G. Jackson, G.A. Lawrance, A.M. Sargeson, Inorg. Synth. 22 (1983) 105;
[158] N.E. Dixon, G.A. Lawrance, P.A. Lay, A.M. Sargeson, Inorg. Chem. 22 (1983) 847;
[159] G.A. Lawrance, A.M. Sargeson, Inorg. Synth. 24 (1986) 279;
[160] P.A. Lay, A.M. Sargeson, Inorg. Synth. 24 (1986) 283;
[161] P.A. Lay, A.M. Sargeson, H. Taube, Inorg. Synth. 24 (1986) 287;
[162] P.A. Lay, A.M. Sargeson, H. Taube, Inorg. Synth. 24 (1986) 291;
[163] D.C. Ware, P.A. Lay, H. Taube, Inorg. Synth. 24 (1986) 299;
[164] C. Diver, G.A. Lawrance, J. Chem. Soc., Dalton Trans. (1988) 931;
[165] N.J. Curtis, G.A. Lawrance, A.M. Sargeson, Inorg. Synth. 24 (1986) 277;
[166] M. Bombín, M.A. Martinez-Zaporta, A. Ramirez, A. Guerro, A.J. Mendez, Thermochim. Acta 224 (1993) 151;
[167] E.J. Kosnic, E.L. McClymont, R.A. Hodder, P.J. Sqattrito, Inorg. Chim. Acta 244 (1996) 253;
[168] M.A. Leonard, P.J. Squattrito, S.N. Dubey, Acta Crystallogr. C55 (1999) 35;
[169] Y. Ohki, Y. Suzuki, T. Takeuchi, A. Ouchi, Bull. Chem. Soc. Jpn. 61 (1988) 393;
[170] C. Couldwell, K. Prout, D. Bobey, R. Taylor, F.J.C. Rossotti, Acta Crystallogr. B34 (1978) 1491;
[171] A. Guerrero-Laverat, A. Ramírez, A. Jerónimo, A. Santos, F. Florencio, S. Martínez-Carrera, S. García-Blanco, Inorg. Chim. Acta 128 (1987) 113;
[172] M.A.S. Aquino, W. Clegg, Q. Liu, A.G. Sykes, Acta Crystallogr. C51 (1995) 560;
[173] K.O. Debevc, C. Pohar, V. Vlachy, J. Soln. Chem. 25 (1996) 787;
[174] B. Sun, Y. Zhao, J.-G. Wu, Q.-C. Yang, G.-X. Xu, J. Molec. Struct. 470 (1998) 63;
[175] S. Cabaleiro-Martinez, J. Castro, J. Romero, J.A. Garcia-Vazquez, A. Sousa, Acta Crystallogr. C56 (2000) e249;
[176] J.S. Haynes, J.R. Sams, R.C. Thompson, Can. J. Chem. 59 (1981) 669;
[177] A.S. Batsanov, J.A.K. Howard, N.S. Moore, M. Kilner, Acta Crystallogr. E57 (2001) m485;
[178] V.P. Kapila, B. Kapila, S. Kumar, Ind. J. Chem. 30A (1991) 908;
[179] P. Bernhard, H.-B. Bürgi, J. Hauser, H. Lehmann, A. Ludi, Inorg. Chem. 21 (1982) 3936;
[180] W. Luginbühl, A. Ludi, A. Raselli, H. Bürgi, Acta Crystallogr. C45 (1989) 1428;
[181] P. Kapoor, P. Wadhawan, S. Tuli, Ind. J. Chem. 29A (1990) 982;
[182] E.J. Kosnic, E.L. McClymont, R.A. Hodder, P.J. Squattrito, Inorg. Chim. Acta 244 (1996) 253;
[183] E.J. Kosnic, E.L. McClymont, R.A. Hodder, P.J. Squattrito, Inorg. Chim. Acta 201 (1992) 143;
[184] K.O. Debevc, C. Pohar, V. Vlachy, J. Soln. Chem. 25 (1996) 787;
[185] M.A.S. Aquino, W. Clegg, Q. Liu, A.G. Sykes, Acta Crystallogr. C51 (1995) 560;
[186] T. Fajinayaga, I. Sakamoto, Pure Appl. Chem. 52 (1980) 1389;

[187] W.G. Jackson, G.A. Lawrance, P.A. Lay, A.M. Sargeson, Aust. J. Chem. 35 (1982) 1561;

[188] J. MacHarrowfield, A.M. Sargeson, B. Singh, J.C. Sullivan, Inorg. Chem. 14 (1975) 2864;

[189] W.G. Jackson, C.M. Beghie, Inorg. Chem. 20 (1981) 1654;

[190] E.A. Boubreaux, L.N. Mulay, Theory and Applications of Molecular Paramagnetism, Wiley, 1962;

[191] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307;

[192] G.M. Sheldrick, SHELX-97. Programs for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, 1997;

[193] G.M. Sheldrick, SADABS- An empirical absorption correction program; Bruker Analytical X-ray Systems, Madison, Wisconsin, 1996;

[194] G.M. Sheldrick, Acta Cryst. C71 (2015) 3;

[195] International Tables for Crystallography Vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992;

[196] D.-F. Li, R. Clérac, S. Parkin, G.-B. Wang, G.T. Yee, S.M. Holmes, Inorg. Chem. 45 (2006) 5251.

[197] A.A. Maryott, E.R. Smith Table of Dielectric Constants of Pure Liquids, National Bureau of Standards Circular 514, 1951;

[198] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, 5th Ed., John Wiley & Sons, New York, 1997;

[199] Y. Tanabe, S. Sugano, J. Phys. Soc. Jpn. 9 (1954) 766;

[200] A.B.P. Lever, Inorganic Electronic Spectroscopy, VCH, New York, 1994;

[201] C.K. Jørgenson, Absorption Spectra and Chemical Bonding in Complexes, Pergamon Press, New York, 1964;

[202] A.B.P. Lever, J. Chem. Educ. 45 (1968) 711;

[203] R.S. Drago, Physical Methods for Chemists, 2nd Ed., Saunders College Publishers, New York, 1992, pp. 735-736.

[204] E.I. Solomon, A.B.P. Lever, Inorganic Electronic Structure and Spectroscopy, vols. I and II, Wiley, New York, 2006;

[205] D.W. Meeks, R.S. Drago, T.S. Piper, Inorg. Chem. 1 (1962) 285;

[206] D.M. Meek, R.S. Drago, T.S. Piper, Inorg. Chem. 1 (1962) 285;

[207] C.K. Jørgenson, Acta Chem. Scand. 9 (1955) 1362;

[208] D.W. Meeks, R.S. Drago, T.S. Piper, Inorg. Chem. 1 (1962) 285;

[209] V. Imhof, R.S. Drago, Inorg. Chem. 4 (1965) 427;

[210] O. Bostrup, C.K. Jørgenson, Acta Chem. Scand. 11 (1957) 1223;

[211] A. Bose, R. Chatterjee, Proc. Phys. Soc. 83 (1963) 23;

[212] E. Konig, Struct. Bond. 9 (1971) 175;

[213] F. Charbonnier, R. Fauer, H. Loiseleur, Acta Crystallogr. 34B (1978) 1504;

[214] P.J. Ferko, J.R. Withers, H. Nguyen, J. Ema, T. Ema, C. Dornhoefer, N.P. Rath, S.M. Holmes, J. Chem. Educ., in press;

[215] J.Y. Jeon, J.H. Park, D.S. Park, S.Y. Park, C.S. Lee, M.J. Go, J. Lee, B.Y. Lee, Inorg. Chem. Commun. 44 (2014) 148;

[216] C. Zitzer, T.W.T. Muesmann, J. Christoffers, M.S. Wickleder, New J. Chem. 39 (2015) 6117;

[217] A. Guerrero-Laverat, A. Ramírez, A. Jerónimo, A. Santos, F. Florencio, S. Martínez-Carrera, S. Garcia-Blanco, Inorg. Chim. Acta 128 (1987) 113;

Table 1. Relative solubilities of {*trans*-[$Co(OTs)_2(DMF)_4$]}·H_2O (**3**) and [$Ni(DMF)_4$][OTs]$_2$ (**4**) in various organic solvents (ε = dielectric constant).

cmpd	**benzene** (2.3)	**diethyl ether** (4.3)	**chloroform** (4.8)	**tetrahydrofuran** (7.5)	**ethyl acetate** (6.0)	**dichloromethane** (9.1)	**pyridine** (12.3)	***tert*-butyl alcohol** (12.5)	**1,2-diaminoethane** (14.2)	**2-propanol** (18.3)
3	●	🟥	●	○	○	●	🟩	🟥	🟥	●
4	🟩	🟥	●	○	○	●	🟩	🟥	🟥	●
	1-propanol (20.1)	**acetone** (20.7)	**ethanol** (24.6)	**2,4-pentanedione** (25.7)	**methanol** (32.6)	**nitromethane** (35.8)	**acetonitrile** (37.5)	**dimethylfomamide** (38.3)	**dimethylsulfoxide** (47)	**water** (78.5)
3	●	●	○	○	🟩	●	○	🟩	○	🟩
4	●	●	○	○	🟩	●	●	🟩	○	🟩

● = precipitation; 🟩 = soluble; ○ = slightly soluble; 🟥 = insoluble.

Table 2. Crystallographic data for $\{trans\text{-}Cr(OTs)_2(DMF)_2\}_n$ (**1**-H_2O), *trans*-$[Fe(OTs)_2(DMF)_4]$ (**2**-H_2O), *trans*-$[Co(OTs)_2(DMF)_4]$ (**3**), $[Ni(DMF)_6][OTs]_2$ (**4**+2DMF), and *trans*-$[Fe(OTs)_2(DMF)_2(OH_2)_2]$ (**5**).

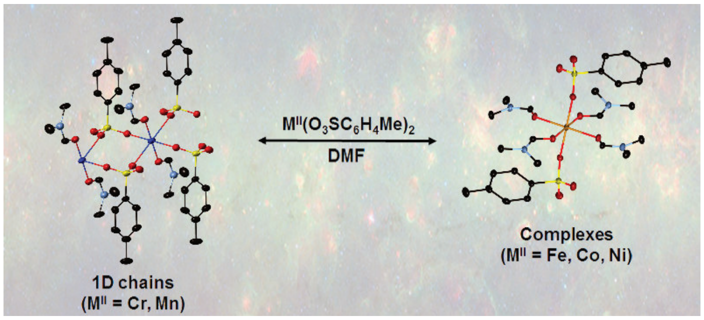
	1	**2**	**3**	**4**	**5**
formula	$C_{20}H_{28}CrN_2O_8S_2$	$C_{26}H_{42}FeN_4O_{10}S_2$	$C_{26}H_{42}CoN_4O_{10}S_2$	$C_{32}H_{56}N_6NiO_{12}S_2$	$C_{20}H_{32}FeN_2O_{10}S_2$
formula weight	540.56	690.61	693.69	839.66	580.45
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
temp., K	90.0(2)	100(2)	90.0(2)	100(2)	100(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	P-1
a, Å	14.5952(5)	7.8561(7)	7.8465(1)	9.5355(7)	6.3485(1)
b, Å	5.2241(2)	24.663(2)	24.5324(3)	22.696(1)	8.6866(2)
c, Å	17.0215(8)	8.8289(7)	8.7975(1)	9.3886(6)	12.1192(2)
α, °					87.850(1)
β, °	112.454(2)	111.155(3)	110.926(6)	94.884(4)	84.329(1)
γ, °					76.869(1)
V, Å^3	1199.44(8)	1595.4(2)	1581.76(3)	2024.5(2)	647.57(2)
Z	2	2	2	2	1
ρ_c, g cm^{-3}	1.497	1.438	1.456	1.377	1.488
μ, mm^{-1}	0.699	0.662	0.734	0.647	0.798
R_1^a	0.0515	0.0299	0.0368	0.0324	0.0305
wR_2^a	0.1195	0.0754	0.0937	0.0701	0.0792

[a] $I \geq 2\sigma(I)$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2=\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

Table 3. Selected Bond Distances (Å) and Angles (°) for {*trans*-Cr(OTs)$_2$(DMF)$_2$}$_n$ (**1**-H$_2$O), *trans*-[Fe(OTs)$_2$(DMF)$_4$] (**2**-H$_2$O), *trans*-[Co(OTs)$_2$(DMF)$_4$] (**3**), [Ni(DMF)$_6$]-[OTs]$_2$ (**4**+2DMF), and *trans*-[Fe(OTs)$_2$(DMF)$_2$(OH$_2$)$_2$] (**5**).

1		**2**		**3**		**4**		**5**	
Cr1-O2A	2.076(2)	Fe1-O1	2.1237(7)	Co1-O1	2.028(1)	Ni1-O1	2.051(1)	Fe1-O1	2.1498(9)
Cr1-O3	2.403(2)	Fe1-O2	2.1574(7)	Co1-O1A	2.231(2)	Ni1-O2	2.062(1)	Fe1-O2	2.0804(7)
Cr1-O4	2.038(2)	Fe1-O3	2.0958(7)	Co1-O1B	2.049(1)	Ni1-O3	2.042(2)	Fe1-O3	2.1428(8)
S1-O1	1.444(2)	S1-O3	1.4793(8)	S1-O1	1.490(2)	O1-C1	1.248(2)	S1-O3	1.4720(9)
S1-O2	1.482(2)	S1-O4	1.4466(8)	S1-O2	1.367(2)	C1-N1	1.317(2)	S1-O4	1.4578(9)
S1-O3	1.444(2)	S1-O5	1.4532(8)	S1-O3	1.579(2)	S1-O4	1.453(2)	S1-O5	1.4530(9)
S1-C5	1.773(3)	S1-C7	1.774(1)	S1-C1	1.743(2)	S1-O5	1.456(2)	S1-C1	1.767(1)
O4-C8	1.253(4)	O1-C1	1.243(1)	O1A-C1A	1.305(3)	S1-O6	1.453(2)	O2-C8	1.246(1)
C8-N1	1.318(4)	C1-N1	1.327(1)	C1A-N1A	1.435(3)	S1-C10	1.778(2)	C8-N1	1.323(1)
Cr1···Cr1A	5.224(2)	Fe1···Fe1A	7.847(1)	Co1···Co1A	7.846(3)	Ni1···Ni1A	9.535(2)	Fe1···Fe1A	6.348(1)
S1···S1A	4.579(2)	S1···S1A	6.667(1)	S1···S1A	6.495(3)	S1···S1A	8.997(2)	S1···S1A	6.686(1)
O4-Cr1-O2A	89.85(8)	O1-Fe1-O2	88.34(3)	O1-Co1-O1A	83.74(6)	O1-Ni1-O2	92.86(5)	O1-Fe1-O2	93.10(3)
O3-Cr1-O2A	87.00(1)	O1-Fe1-O3	89.28(3)	O1-Co1-O1B	87.56(6)	O1-Ni1-O3	90.90(5)	O1-Fe1-O3	88.83(3)
O1-S1-O2	110.3(1)	O2-Fe1-O3	90.42(3)	O1A-Co1-O1B	92.44(6)	O2-Ni1-O3	89.43(5)	O2-Fe1-O3	93.18(3)
O1-S1-O3	114.8(1)	O3-S1-O4	113.23(5)	O1-S1-O2	108.48(9)	O4-S1-O5	112.67(9)	O3-S1-O4	111.52(5)
O1-S1-C5	106.5(1)	O3-S1-O5	110.32(5)	O1-S1-O3	114.94(9)	O4-S1-O6	113.38(9)	O3-S1-O5	111.59(5)
O2-S1-O3	112.8(1)	O4-S1-O5	114.73(5)	O2-S1-O3	116.5(1)	O5-S1-O6	113.20(9)	O4-S1-O5	113.79(5)
O4-C8-N1	124.1(3)	O3-S1-C7	104.91(4)	O1-S1-C1	104.55(9)	O4-S1-C10	104.58(9)	O3-S1-C1	106.94(5)
S1-O2-Cr1	133.6(1)	O1-C1-N1	123.80(9)	O1A-C1A-N1A	129.6(2)	O1-C1-N1	124.4(2)	O2-C8-N1	123.1(1)
Cr1-O3-S1	142.662	Fe1-O3-S1	137.22(4)	Co1-O1-S1	134.19(9)	Ni1-O1-C1	123.7(2)	Fe1-O3-S1	134.45(5)
Cr1-O2A-S1A	133.616	Fe1-O1-C1	122.67(6)	Co1-O1A-C1A	131.0(2)	Ni1-O2-C4	123.1(2)	Fe1-O2-C8	132.58(7)
		Fe1-O2-C4	125.14(6)	Co1-O1B-C1B	118.4(1)	Ni1-O3-C7	125.3(2)		

TOC



The structures, magnetism, and spectroscopic properties of several 3*d* transition metal *p*-toluenesulfonate complexes and chains are described. A one-dimensional chain {*trans*-Cr^{II}(DMF)$_2$(OTs)$_2$}$_n$·*n*H$_2$O (**1**) and mononuclear complexes of {*trans*-[M^{II}(OTs)$_2$(DMF)$_4$]}·*n*H$_2$O (M^{II} = Fe, **2**; Co, **3**; *n* = 1, 0) and [Ni^{II}(DMF)$_4$][OTs]$_2$ (**4**) stoichiometry are described.