Two new nickel–dmit-based molecular conductors based on heteroleptic polymetallic complexes: synthesis, structures and electrical properties

Tianlu Sheng, Xintao Wu,* Wenjian Zhang, Quanming Wang, Xiancheng Gao and Ping Lin

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fjuian, 350002, PR China

Two heteroleptic dmit complexes of polynuclear nickel(II), $[NEt_4]_2[Ni_5(edt)_4(dmit)_2]$ and $[AsPh_4]_2[Ni_3(pdt)_2(dmit)_2]\cdot0.5MeOH$ (dmit = 2-thione-1,3-dithiole-4,5-dithiolate, H_2edt = ethane-1,2-dithiol, H_2pdt = propane-1,2-dithiol) are synthesized and characterized by X-ray crystallography and display room-temperature conductivities of 1.75×10^{-4} and 1.52×10^{-5} S cm^{-1}; this is the first report of semiconducting heteroleptic dmit complexes consisting of more than two nickel(II) centres.

During the search for new complexes with novel electric properties, metal complexes of the dmit ligand have received considerable attention[1,2] since some of them were reported to exhibit conductivities and even superconductivities.[3–7] Some non-planar metal–dmit complexes have also been reported to exhibit high conductivities.[8] Recently, it has been shown that intermolecular interactions in transition metal bis(dithiolate) complexes of this type are also important for the assembly of molecular ferromagnets.[9] A large number of metal–dmit complexes have been synthesized and structurally characterized but many of them are homoleptic. To our knowledge, heteroleptic polymetallic complexes of dmit in particular, are rare. These types of complexes reported in the literature are restricted to $[NBu_4]_2[Ni_2(C_2S_4)(dmit)_2]$,[10] $[Au_4(dmit)_2(Ph_2PCH_2PPh_2)_2]$ and $[Au_3(PPh_3)_3(dmit)]$.[11] We have now investigated whether dithiolate can be used as a bridging ligand to synthesize heteroleptic polymetallic complexes with dmit. As two examples, two heteroleptic nickel(II) derivatives $[NEt_4]_2[Ni_5(edt)_4(dmit)_2]$ **1** and $[AsPh_4]_2[Ni_3(pdt)_2(dmit)_2]\cdot0.5MeOH$ **2**, were formed by using edt or pdt as bridging ligands; this is the first report of heteroleptic dmit complexes consisting of more than two nickel(II) centres.

4,5-Bis(benzoylthio)-1,3-dithiole-2-thione (prepared according to the detailed procedures described by Steimecke *et al.*[12]) (0.408 g, 1.0 mmol) was dissolved in a methanol solution (30 ml) containing sodium (0.046 g, 2.0 mmol). To the resulting purple–red solution of Na_2dmit was added H_2edt (0.06 ml, 1.4 mmol) and then $NiCl_2\cdot6H_2O$ (0.24 g, 1.0 mmol) to give a purple solution. After stirring for 6 h at room temp. a methanol solution (10 ml) of NEt_4Br (0.2 g, 1.0 mmol) was added leading to the precipitation of a purple product. This was collected by filtration and redissolved in dmf (10 ml); then it was filtered after stirring for several minutes. This filtrate was diffused with Et_2O at room temp. for ten days, after which 0.12 g of black crystals of **1** were obtained. The preparation of complex **2** was similar to that of **1**, H_2edt and NEt_4Br being replaced by H_2pdt and $AsPh_4Cl$, respectively. The red precipitate was collected by filtration and redissolved in Me_2CO (10 ml) and then filtered after stirring for several min. The filtrate was diffused with Et_2O at room temp. for ten days after which 0.35 g of black crystals of **2** were obtained.†

The structures of **1** and **2** were established by single-crystal X-ray diffraction analysis‡ and reveal the edt or pdt ligands in bridging modes chelated to Ni atoms and dmit ligands coordinated to edge Ni atoms. The anions of **1** and **2** together with selected bond parameters are depicted in Figs. 1 and 2. In **1**, the anion occupies a crystallographic inversion center, the five Ni atoms are bridged by four edt ligands, Ni(1), Ni(2) and Ni(2′) are square-planar coordinated to four S atoms of edt ligands and both the edge Ni atoms are square-planar coordinated to two S atoms of edt ligands and to two S atoms from one dmit ligand. From the configuration of the five Ni atoms and two dmit ligands, the anion can be described as consisting of an $Ni_3(edt)_4^{2-}$ unit to which are *trans* attached two $Ni(dmit)_2$ fragments, the angle Ni(1)–Ni(2)–Ni(3) [Ni(1)–Ni(2′)–Ni(3′)] being 102.83°. The Ni···Ni bond distances are 2.852(1) and 2.817(1) Å and are slightly shorter than that in $[PPh_4]_2[Ni_2(edt)_3]$ **3**[17] [2.914(1) Å] and comparable to the distances in $[PPh_4]_2[Ni_3(edt)_4]$ **4**[18] [2.856(1) Å]. The Ni–S bond distances vary from 2.151(3) to 2.227(3) Å which are comparable to the Ni–S bond distances in **3**[17] [2.158(2)–2.221(2) Å] and **4**[18] [2.174(1)–2.210(1) Å] as well as

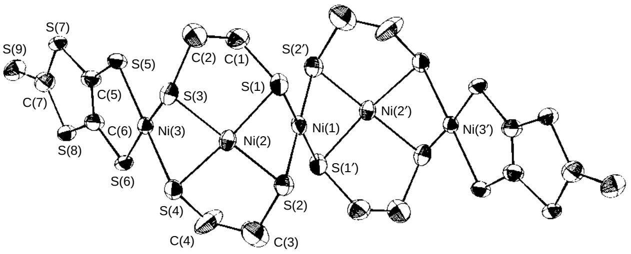

Fig. 1 ORTEP diagram of the anion of **1** (25% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Ni(1)–Ni(2) 2.852(1), Ni(2)–Ni(3) 2.817(1), Ni(1)–S(1) 2.213(3), Ni(1)–S(2) 2.215(3), Ni(2)–S(1) 2.169(3), Ni(2)–S(2) 2.151(3), Ni(2)–S(3) 2.159(3), Ni(2)–S(4) 2.160(3), Ni(3)–S(3) 2.222(3), Ni(3)–S(4) 2.227(3), Ni(3)–S(5) 2.174(3), Ni(3)–S(6) 2.171(3); Ni(1)–Ni(2)–Ni(3) 102.83.

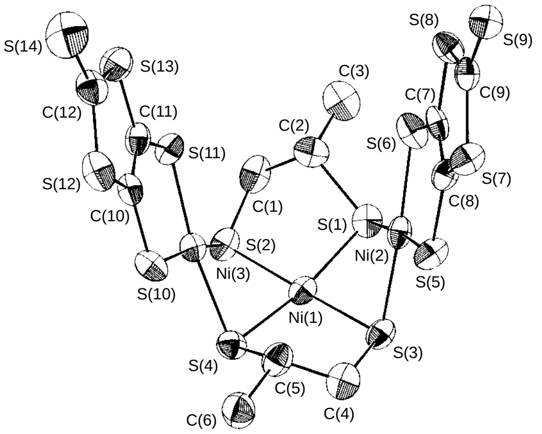

Fig. 2 ORTEP diagram of the anion of **2** (25% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Ni(1)–Ni(3) 2.792(2), Ni(1)–Ni(2) 2.812(2). Ni(1)–S(1) 2.143(3), Ni(1)–S(2) 2.149(3), Ni(1)–S(3) 2.156(3), Ni(1)–S(4) 2.184(3), Ni(2)–S(5) 2.161(3), Ni(2)–S(6) 2.167(3), Ni(2)–S(1) 2.244(3), Ni(2)–S(3) 2.245(3), Ni(3)–S(11) 2.151(3), Ni(3)–S(10) 2.176(3), Ni(3)–S(2) 2.223(3), Ni(3)–S(4) 2.240(3); Ni(3)–Ni(1)–Ni(2) 102.47(5).

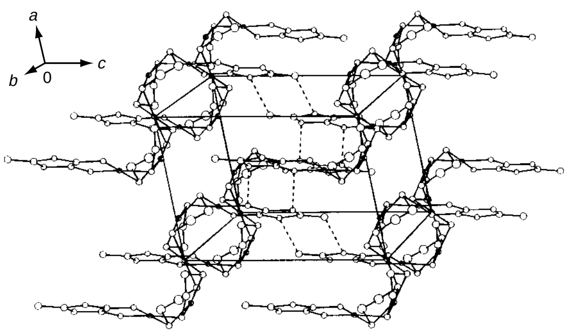

Fig. 3 The packing of **1** in the crystal. Dashed lines indicate non-bonded S···S contacts < 3.7 Å, the cations are omitted for clarity.

in $[AsPh_4]_2[Ni_2(S_2C_4)\{S_2C_2S_2C_2(CO_2Me)_2\}_2]$[19] and $[NBu_4]_2[Ni_2(C_2S_4)(dmit)_2]$.[10]

As shown in Fig. 2, the geometry around the Ni atoms in **2** is similar to those in **1**, the three Ni atoms adopt a V shape with the angle Ni(2)–Ni(1)–Ni(3) being 102.47°. In contrast to **1**, complex **2** can be achieved as an $Ni(pdt)^{2-}$ unit to which two $Ni(dmit)_2$ fragments are *cis* bonded. Compared to **1**, the Ni···Ni bond distances [Ni(1)–Ni(2) 2.812(2), Ni(1)–Ni(3) 2.792(2) Å] are slightly shorter, whereas the Ni–S bond lengths are almost the same as those in **1**.

In the crystal of complex **1** (as shown in Fig. 3), the anions interact with each other through S···S contacts of < 3.7 Å between the thiole and thione groups or the thiole and thiole groups of the dmit ligands on adjacent molecules to form a two-dimensional molecular interaction net. However, in the crystal of complex **2**, no S···S contacts < 3.7 Å are observed (the shortest intermolecular S···S distance is 3.92 Å); this may result from using the larger $AsPh_4^+$ ion.

The electrical conductivities of complexes **1** and **2** were measured with pressed pellets (two probe). Both complexes show semiconducting behaviour with room-temperature conductivities of 1.75×10^{-4} and 1.52×10^{-5} S cm^{-1}, respectively. The fact that the conductivity of **1** is higher than that of **2** may be the result of shorter intermolecular non-bonded S···S contacts.

This research was supported by State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, and the Science Foundation of Nation and Fujian Province.

Footnotes and References

* E-mail: wxt@ms.fjirsm.ac.cn

† *Spectroscopic data*: for **1**: IR (KBr pellet: ν/cm^{-1}): ν(Ni–S) 338.2s, 316.7m, 472.1s, 514.6s; ν(C–S) and ν(C=S) 838.3s, 911.1s, 998s, 1024.2s, 1049s. UV–VIS (dmf solution): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 275 (4.2×10^4), 290 (4.62×10^4), 320 (4.09×10^4), 430 (1.12×10^4), 530 (2.2×10^4) (Found: C, 26.53; H, 4.18; N, 2.82; Ni, 22.20. Calc. for $C_{30}H_{56}N_2Ni_5S_{18}$: C, 27.39; H, 4.29; N, 2;13; Ni, 22.31%.)

For **2**: IR (KBr pellet: ν/cm^{-1}): ν(Ni–S) 364.4m, 465.9s, 476.0s, 515.8m; ν(C–S) and ν(C=S) 857.3w, 857.4m, 915.1s, 997.3s, 1023.6s, 1049.1s, 1079.7s. UV–VIS (dmf solution): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 293 (3.3×10^4), 310 (3.4×10^{-4}), 366 (1.4×10^4), 424 (2.2×10^3), 517 (1.7×10^4). (Found: C, 46.76; H, 3.62; Ni, 11.21. Calc. for $C_{60.5}H_{54}As_2Ni_3O_{0.5}S_{14}$: C, 46.47; H, 3.48; Ni, 11.26%).

‡ *Crystal data*: **1**: $C_{30}H_{56}N_2Ni_5S_{18}$, M_r = 1315.32, triclinic, space group $P\bar{1}$, a = 9.407(4), b = 11.665(3), c = 12.777(3), α = 106.45(2), β = 101.54(3), γ = 100.79(3)°, U = 1272(1) Å^3, Z = 1, D_c = 1.72 g cm^{-3}, T = 296 K, λ(Mo-Kα) = 0.710 73 Å, θ range 0–25°. Enraf-Nonius CAD4 diffractometer, ω–2θ scans. 4468 reflections are unique, 2821 reflections with $I > 3.0\sigma(I)$ were used in the refinement and used to calculate R and R_w. The last successful full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms (250 variables) converged to R = 0.058, R_w = 0.062 $\{w = [\sigma^2(F_o)^2 + (0.020F_o)^2 + 1.000]^{-1}\}$, the final maximum residual electron density is 0.80 e Å^{-3}. The positions of hydrogen atoms were calculated in ideal positions and not used in the least-squares refinement. The structure was solved by direct methods, and the positions of Ni atoms were obtained from E maps. The remaining non-H atoms were located from successive difference Fourier maps. The refinement of the structure was performed by full-matrix least-squares techniques on F using MolEN.[13] Data were corrected for absorption with program DIFABS.[14]

2: $C_{60.5}H_{54}As_2Ni_3O_{0.5}S_{14}$, M_r = 1563.85, triclinic, space group $P\bar{1}$, a = 14.3284(2), b = 14.9487(3), c = 17.2496(3), α = 102.886(1), β = 101.898(1), γ = 102.687(1)°, U = 3385(2) Å^3, Z = 2, D_c = 1.534 g cm^{-3}, T = 293 K, λ(Mo-Kα) = 0.710 73 Å, θ range 1.90–23.2°. Siemens Smart CCD diffractometer, ω scans. 9438 unique reflections were used in the refinement and 6615 reflections with $I > 2.0\sigma(I)$ used to calculate R and R_w. The last successful full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms except solution molecule (720 variables) converged to R = 0.0739, R_w = 0.2085 $\{w = [\sigma^2(F_o)^2 + (0.1355P)^2 + 4.7414P]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3\}$. The solvent molecule is disordered. The final maximum residual electron density is 2.477 e Å^{-3}, lying 1.073 Å from Ni(1). The positions of hydrogen atoms were calculated in ideal positions and not used in the least-squares refinement. The structure was solved by direct methods, and the positions of three Ni atoms were obtained from E maps. The remaining non-H atoms were located from successive difference Fourier maps. The refinement of the structure was performed by full-matrix least-squares techniques on F^2 using SHELXL-93.[15] Data were corrected for absorption with SADABS.[16] CCDC 182/702.

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Received in Cambridge, UK, 23rd September 1997; 7/06685I