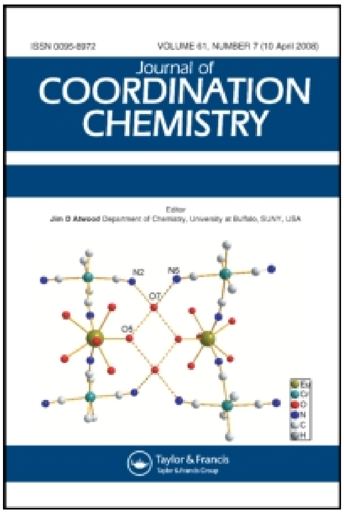

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Synthesis, crystal structure and magnetic property of a maleonitriledithiolate nickel(III) complex containing an ammonium crown ether cation

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Synthesis, crystal structure and magnetic property of a maleonitriledithiolate nickel(III) complex containing an ammonium crown ether cation

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The synthesis, molecular structure and spectroscopic and magnetic properties of $(NH_4)_2$(15-crown-5)$_3$[Ni(mnt)$_2$]$_2$ (mnt = maleonitriledithiolate dianion) are reported. The most notable structural feature of $(NH_4)_2$(15-crown-5)$_3$[Ni(mnt)$_2$]$_2$ is that the ions form a stacked structure with well-separated columns along the *c* and *a* axes. Variable temperature magnetic susceptibility measurements indicate strong antiferromagnetic interactions in the complex.

Keywords: Maleonitriledithiolate; 15-Crown-5; Crystal structure; Dimer; Nickel(III) complex

1. Introduction

Recently, certain supramolecular structures formed through non-covalent interactions have increasingly attracted attention in view of their applications in crystal engineering [1]. The supramolecular cation (SC$^+$) structures involve an ionic crown ether complex linked by non-covalent interactions to [Ni(dmit)$_2$]$^-$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate). Compounds of the latter possess highly electrically conducting properties [2–4]. Supramolecular cations are favourable for the construction of novel d–π spin systems because of their ability to regulate [Ni(dmit)$_2$]$^-$ configurations in a crystal, thus affecting their magnetic function [5, 6]. In the present article, we report the synthesis, molecular structure and spectroscopic and magnetic properties of $(NH_4)_2$(15-crown-5)$_3$[Ni(mnt)$_2$]$_2$ (mnt = maleonitriledithiolate dianion).

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2. Experimental

2.1. Physical measurements

IR spectra (KBr discs) were recorded on a Bruker Vector 22 spectrophotometer in the 400–4000 cm^{-1} region. Electronic spectra were recorded with a Shimadzu UV-3100 spectrophotometer. Elemental analyses (C, H, N) were obtained using a Perkin-Elmer 240C instrument. Magnetic susceptibility data using powdered polycrystalline samples were collected over the temperature range 2–300 K using a Quantum Design MPMS-5S SQUID magnetometer, and data were corrected for diamagnetism of constituent atoms using Pascal's constants.

2.2. $(NH_4)_2(15\text{-crown-}5)_3[Ni(mnt)_2]_2$

All reagents and solvents were of A.R. grade and used without further purification. Disodium maleonitriledithiolate (Na_2mnt) was prepared using a synthetic procedure described in the literature [7]. $[(n\text{-}Bu)_4N][Ni(mnt)_2]$ was prepared according to a published procedure [8]. A solution of $[(n\text{-}Bu)_4N][Ni(mnt)_2]$ (73.7 mg, 0.127 mmol) in acetone : water (70 : 30, v : v) was passed through an ion-exchange column containing Dowex 50W X8 in the acid form. An aqueous solution of NH_4Cl (13.7 mg, 0.255 mmol) was added to the resulting solution of $H_2[Ni(mnt)_2]$, then an acetone solution of 15-crown-5 (56.1 mg, 0.255 mmol) was added. The solution was allowed to evaporate at room temperature to give black prismatic crystals, which were suitable for single-crystal X-ray diffraction studies. Anal. Calcd for $C_{46}H_{68}N_{10}Ni_2O_{15}S_8$ (%): C 40.18; H 4.98; N 10.19. Found: C 40.23; H 5.01; N 10.21. IR (cm^{-1}): 3213m, 2913m, 2873m, 2209s, 1442m, 1421m, 1356m, 1307w, 1246m, 1118s, 1039m, 1026m, 939m, 854m, 516w, 500w.

2.3. X-ray crystallography

Diffraction experiments were carried out on a Bruker AXS SMART APEX CCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXTL [9]. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were included in the refinement in calculated positions, riding on their carrier atoms. A summary of data collection and structure refinement details is given in table 1.

3. Results and discussion

3.1. Crystal structure

Selected bond lengths and angles for $(NH_4)_2(15\text{-crown-}5)_3[Ni(mnt)_2]_2$ are summarized in table 2. An ORTEP drawing of the compound with labelling of the atoms is shown in figure 1. The asymmetric unit consists of two NH_4 cations, three 15-crown-5 molecules and two $[Ni(mnt)_2]^-$ anions. In $[Ni(mnt)_2]^-$, Ni(III) is coordinated to four sulfur atoms of two ligands and exhibits square planar coordination geometry. The CN groups of the ligand are bent away from the coordination plane defined by the four sulfur atoms. The five-membered chelate rings are slightly puckered. The average

Table 1. Crystal data and structure refinement details.

Formula	$(NH_4)_2(15\text{-crown-}5)_3[Ni(mnt)_2]_2$
Empirical formula	$C_{46}H_{68}N_{10}Ni_2O_{15}S_8$
Formula weight	1375.00
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	15.088(4)
b (Å)	15.349(4)
c (Å)	16.709(4)
α (°)	102.03(4)
β (°)	97.46(5)
γ (°)	119.21(4)
V (Å^3)	3179.1(14)
Z	2
D_{calc} (g cm^{-3})	1.436
μ(Mo Kα) (mm^{-1})	0.922
T (K)	293
F(000)	1436
Crystal size (mm^3)	$0.20 \times 0.15 \times 0.15$
θ range for data collection (°)	1.84–26.00
Index ranges	$-17 \le h \le 17$, $-18 \le k \le 17$, $-19 \le l \le 17$
Reflections collected	15832
Independent reflections	10977
Observed data	7654
R(int)	0.047
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10977/0/730
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0606$, $wR_2 = 0.1243$
R indices (all data)	$R_1 = 0.1119$, $wR_2 = 0.1442$
Goodness-of-fit on F^2	1.07

Ni–S bond distance is 2.139(5) Å and the average S–Ni–S bond angle in the five-membered rings is 90.00(6)°. These values are in agreement with those reported for related complexes [10]. The most notable structure feature of $(NH_4)_2$ $(15\text{-crown-}5)_3[Ni(mnt)_2]_2$ is that the anions and large supramolecular cations form a stacked structure with well-separated columns along the *c* and *a* axes. Overlap of pairs of $[Ni(mnt)_2]^-$ anions gives a metal-over-metal, dimeric configuration, while (distant) overlap between dimers is of the metal-over-sulfur type. Nearest S···S, S···Ni and Ni···Ni distances are 3.813, 3.831 and 4.056 Å in the the dimer, respectively. These distances are larger than the sum of the van der Waal radii of the corresponding atoms. There are no significant intermolecular interactions between neighbouring dimers.

The NH_4^+ ion in the sandwich-type dimers interacts with 15-crown-5 units through N–H···O hydrogen bonding and N···O contacts, resulting in hexa-coordination for N9 and hepta-coordination for N10. The coordination mode of N atoms in the supramolecular cations is different to found in $NH_4^+(15\text{-crown-}5)_2[Ni(dmit)_2]$ [11]. Hydrogen bond distances for N9–H9D···O1, N9–H9C···O4, N9–H9E···O11^{i}, N9–H9F···O13^{i} and N9–H9E···O15^{i} [symmetry code (i): $x, 1+y, z$] are 2.979(6), 3.011(5), 2.899(4), 2.886(5), and 2.928(5) Å, respectively; distances for N10–H10F···O2^{ii}, N10–H10E···O4^{ii}, N10–H10E···O5^{ii}, N10–H10D···O6, N10–H10C···O8, N10–H10C···O9, N10–H10D···O10 [symmetry code (ii): $1+x, y, z$] z] are 2.945(5), 3.228(6), 2.978(4), 2.945(6), 2.940(5), 2.931(4), 2.924(5) Å, respectively. All are longer than the typical NH_4^+–O hydrogen bond distance (2.87 Å). The six

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Ni1–S1	2.143(1)	Ni2–S5	2.134(1)
Ni1–S2	2.141(1)	Ni2–S6	2.139(1)
Ni1–S3	2.133(1)	Ni2–S7	2.144(1)
Ni1–S4	2.141(1)	Ni2–S8	2.138(1)
S1–C32	1.721(5)	S5–C40	1.689(5)
S2–C33	1.691(5)	S6–C41	1.718(5)
S3–C36	1.671(5)	S7–C44	1.670(5)
S4–C37	1.715(5)	S8–C45	1.702(5)
C32–C33	1.377(7)	C40–C41	1.395(6)
C36–C37	1.392(6)	C44–C45	1.366(6)
C31–C32	1.395(7)	C39–C40	1.454(7)
C33–C34	1.440(7)	C41–C42	1.391(7)
C31–N1	1.149(6)	C39–N5	1.106(6)
C34–N2	1.124(6)	C42–N6	1.135(6)
C35–C36	1.387(7)	C43–C44	1.447(7)
C37–C38	1.422(7)	C45–C46	1.402(7)
C35–N3	1.184(6)	C43–N7	1.133(6)
C38–N4	1.155(6)	C46–N8	1.201(6)
S2–Ni1–S1	92.54(6)	S5–Ni2–S6	92.88(6)
S3–Ni1–S2	87.68(6)	S6–Ni2–S7	87.79(6)
S3–Ni1–S4	92.03(6)	S8–Ni2–S7	92.40(6)
S4–Ni1–S1	87.74(6)	S5–Ni2–S8	86.99(6)
Ni1–S1–C32	103.3(2)	Ni2–S5–C40	103.4(2)
Ni1–S2–C33	103.6(2)	Ni2–S6–C41	103.8(2)
Ni1–S3–C36	104.4(2)	Ni2–S7–C44	103.3(2)
Ni1–S4–C37	103.9(2)	Ni2–S8–C45	102.7(2)

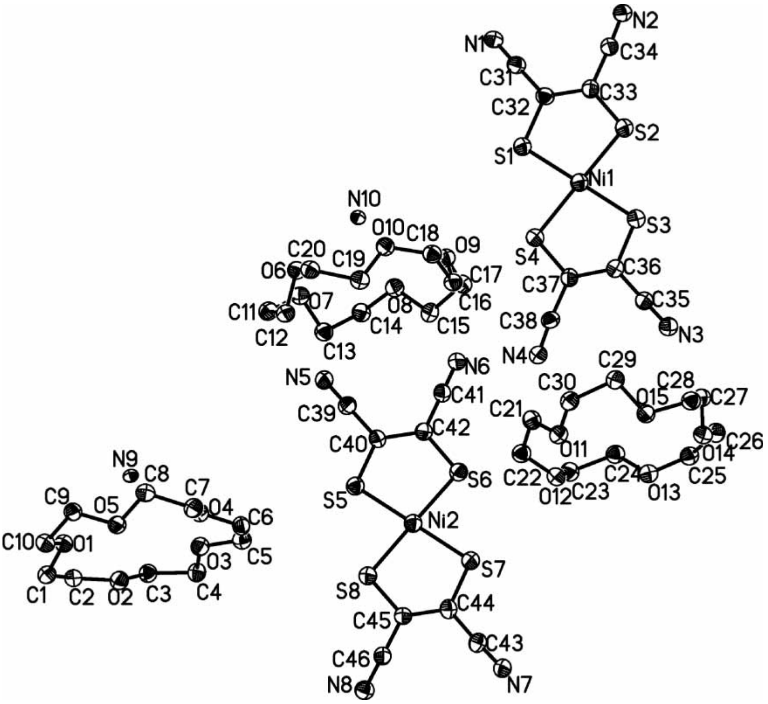

Figure 1. ORTEP view of the compound with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

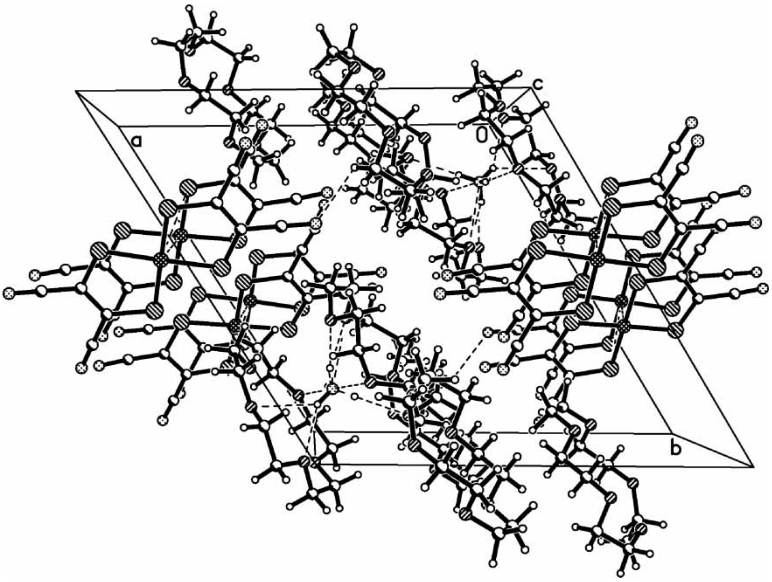

Figure 2. Packing diagram along the *a* axis.

contacts N9···O1 (2.888 Å), N9···O3 (2.986 Å), N10···O6 (2.945 Å), N10···O8 (2.940 Å), N10···O9 (2.931 Å), N10···O10 (2.942 Å) are shorter than the sum of the van der Waals radius of oxygen and the ionic radius of NH_4^+ (3.00 Å). Thus, the supramolecular cations have subtle, loose structures. The deviation of N9 from the least-squares plane defined by O1/O2/O3/O4/O5 is 2.1720 Å, and the corresponding deviation of N10 from O6/O7/O8/O9/O10 is 1.6794 Å. There are C29–H29A···S8^{ii} interactions between the anion and the cation columns, with C29–S8^{ii} being 3.245(8) Å and H29A···S8^{ii} 2.5600 Å. The interactions are important for the stability of the structure, as shown in figure 2.

3.2. *Spectroscopic properties*

The asymmetrical stretching vibration, v(C≡N), appears as an intense single band at 2209 cm^{-1}. Bands at 1442 (1421), 1039 (1026), 939 cm^{-1} can be attributed to *v*(C=C), *v*(C=S) and *v*(C–S) of the mnt^{2-} ligand [12–14]. The strong band at 1118 cm^{-1} can be attributed to *v*(C–O–C) of 15-crown-5 [15]. In addition, the compound exhibits a broad band in the 3000–3500 cm^{-1} region, due to hydrogen-bonded *v*(O–H) and *v*(N–H), and may also include *v*(C–H).

The electronic spectrum of $(NH_4)_2(15\text{-crown-5})_3[Ni(mnt)_2]_2$ was measured in acetone solution in the region 280 to 1100 nm. All bands are attributed to the anions. Characteristic bands at 324, 482 and 865 nm are assigned as $L(\pi) \rightarrow L(\pi^*)$, $L(\delta) \rightarrow M$ and $L(\pi) \rightarrow M$ transitions, respectively, in line with those of $[(n\text{-Bu})_4N]$ $[Ni(mnt)_2]$ [16].

3.3. *Magnetic property*

The temperature dependence of magnetic susceptibility of the complex was measured at an applied field of 2000 Oe. A plot of χ_m *versus T* for the compound is displayed

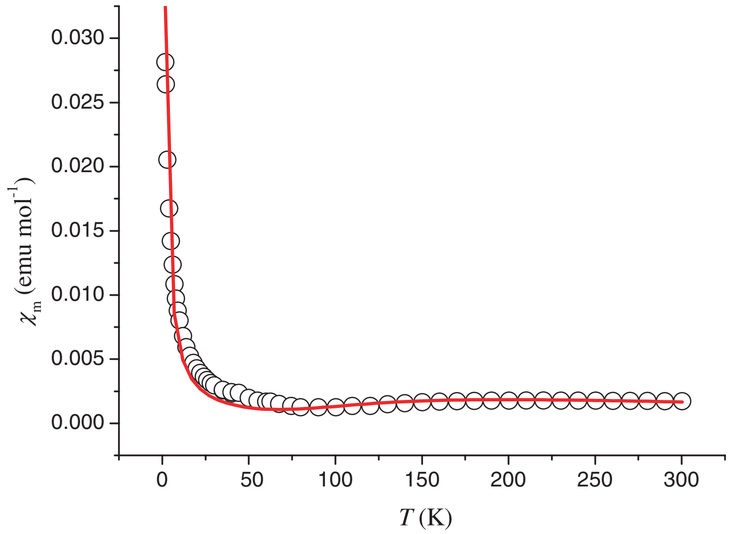

Figure 3. Plot of χ_m *versus* T for the complex. The solid line represents the best fit.

in figure 3, where χ_m is the magnetic susceptibility per nickel atom, corrected for diamagnetic contributions. At 300 K, $\chi_m T$ is estimated as 0.517 emu K mol^{-1}, significantly less than that of a spin-only value of $S = 1/2$ spin per formula unit. This indicates antiferromagnetic exchange between neighbouring Ni(III) ions. The magnetic system can be interpreted using the Heisenberg–Dirac–van Vleck $S_A = S_B = 1/2$ spin-coupled dimer model ($H \cong -2JS_A \cdot S_B$). The expression of magnetic susceptibility of the compound is

$$\chi_m = \frac{2Ng^2\beta^2}{kT} \times \frac{1}{3 + \exp(-2J/kT)} \times (1 - \rho) + \frac{Ng^2\beta^2}{2kT}\rho$$

where N, g, β, k, ρ and T have their usual meanings [17, 18]. A least-squares fit to the susceptibility data gave $J = -246.3\,\text{cm}^{-1}$, $R = 1.8 \times 10^{-6}$ ($R = \sum(\chi_{\text{m calc}} - \chi_{\text{m obs}})^2 / \sum\chi^2_{\text{m obs}}$ and $\rho = 0.07817$, fixing g at 2.0. The J value is indicative of strong antiferromagnetic exchange coupling.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 255331. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: ccdc.cam.ac.uk).

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