Crystal structure of tetra-*n*-butylammonium (1,3-dithiol-2-thione-4,5-dithiolato)-(diethyldithiocarbamato-*S*,*S*′)-nickelate(II), $(C_{16}H_{36}N)(C_8H_{10}NNiS_7)$

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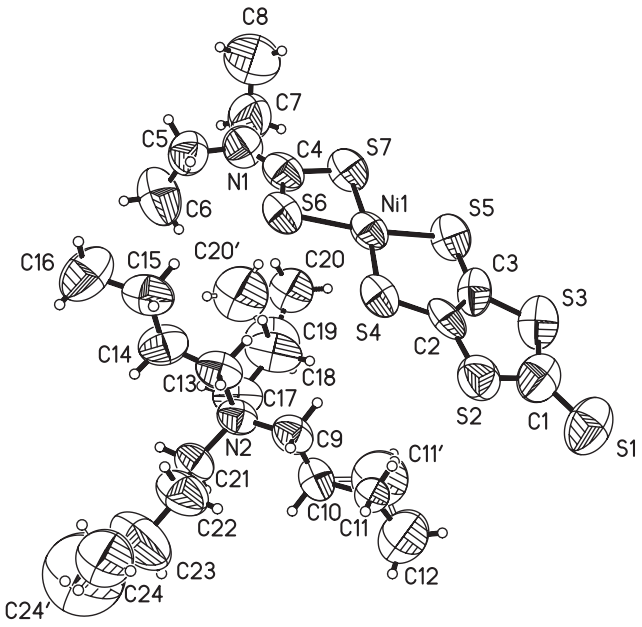

Abstract

$C_{24}H_{46}N_2NiS_7$, monoclinic, *C*1*c*1 (No. 9), *a* = 8.846(2) Å, *b* = 24.702(6) Å, *c* = 15.392(3) Å, β = 95.12(1)°, *V* = 3349.9 Å^3, *Z* = 4, $R_{gt}(F)$ = 0.059, $wR_{ref}(F^2)$ = 0.166, *T* = 293 K.

Source of material

4,5-bis(benzoylthio)-1,3-dithiol-2-thione was treated with an excess of sodium methylate in MeOH under nitrogen at room temperature with stirring. To the resulting red solution, sodium diethyldithiocarbamate, $NiCl_2 \cdot 6H_2O$ and tetra-*n*-butylammonium bromide in MeOH were added. The obtained red precipitate was recrystallized from CH_2Cl_2/$(CH_3)_2CHOH$ in air to produce large platelet crystals. IR data are included in the deposited CIF file.

Experimental details

It was checked by PLATON [1] that the title structure is not consistent with space group *C*2/*c* (no symmetric centre relations between the coordinates of independent atoms). Moreover, the mean absolute value of E^2–1 is 0.741 (expected 0.968 and 0.736 for centrosymmetric and non-centrosymmetric space groups, respectively) and CFOM = 1.24 for *Cc* space group (*E* is the normalized structure factor).

Discussion

In the course of searching for new complexes with novel electric properties, dmit complexes have received considerable attention [2]. Although unsymmetrical donors, such as methylenedithiotetrathiafulvalene, have enriched the domain of the organic conductors, the reports about unsymmetrical metal complexes, such as [M(dmit)X] type, are relatively few [3,4].

We have prepared the title complex TBA[Ni(dmit)(Et_2dtc)] and determined its structure to be in polar non-centrosymmetric space group *Cc*. Because of the two different chelate ring sizes, the Ni—S bond lengths and S–Ni–S angles are quite different. In the dmit five-membered ring, the Ni—S bond lengths are 2.158(3) Å and 2.172(3) Å, average 2.165(4) Å, which is shorter than that of TBA_2[Ni(dmit)$_2$] (2.216(4) Å) [5], and similar to that of TBA[Ni(dmit)$_2$] [6-8]. In the Et_2dtc chelated four-membered ring, the Ni—S bond lengths are 2.198(4) Å and 2.208(3) Å, identical with those in neutral Ni(Et_2dtc)$_2$ [9]. The S–Ni–S angles are 94.7(1)° and 78.5(1)°, corresponding to the five- and four-membered rings, respectively. The whole [Ni(dmit)(Et_2dtc)]$^-$, except for the terminal C6 and C8 atoms, is roughly coplanar with the largest deviations from the least-squares plane being –0.440(1) Å for terminal S1. Both the Et_2dtc ligand with its terminal C6 and C8 excluded, and the dmit ligand are planar with a dihedral angle 16.7(3)°. Thus the skeleton of the [Ni(dmit)(Et_2dtc)]$^-$ anion shows a bent-plane deviation from a square planar conformation and forms layers approximately parallel to the ($\bar{1}$ 0 1) plane. In a ($\bar{1}$01) sheet, neighbouring anions are glide equivalent making their dipolar moments counteracted each other at *b*-axis direction and leaving the component in glide plane added together. All ($\bar{1}$01) anions layers are identical and the title crystal is characterized by its polar non-centrosymmetry, which originates from the bent-plane structure of the asymmetric anion. There are two disorders in three of the butyl chains of the TBA cation. Because of the separation by the bulky cations, there are no intermolecular interactions between anions. However, there are some notable contacts between the Ni1 and protons on the TBA cation (e.g. *d*(H17A···Ni1) = 3.06(1) Å).

Table 1. Data collection and handling.

Crystal:	red plate, size 0.06 × 0.48 × 0.6 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.31 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3768, 3586
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2229
$N(param)_{refined}$:	307
Programs:	PLATON [1], SHELXTL [10]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
H(5A)	4*a*		0.3041	–0.0186	0.7157	0.143
H(5B)	4*a*		0.3559	0.027	0.7827	0.143
H(6A)	4*a*		0.5632	–0.0227	0.7522	0.256
H(6B)	4*a*		0.5805	0.0362	0.7162	0.256
H(6C)	4*a*		0.5290	–0.0110	0.6523	0.256
H(7A)	4*a*		0.3114	0.0134	0.5523	0.188
H(7B)	4*a*		0.2438	0.0716	0.5357	0.188
H(8A)	4*a*		0.0549	0.0072	0.5096	0.276
H(8B)	4*a*		0.0180	0.0440	0.5880	0.276
H(8C)	4*a*		0.0856	–0.0140	0.6055	0.276
H(9A)	4*a*		0.8609	0.2477	0.9595	0.112
H(9B)	4*a*		0.7631	0.2476	0.8696	0.112
H(10A)	4*a*		0.9685	0.2776	0.7994	0.132
H(10B)	4*a*		1.0750	0.2735	0.8870	0.132
C(11)	4*a*	0.47(6)	0.916(3)	0.3361(4)	0.890(2)	0.07(1)
H(11A)	4*a*	0.47	0.8097	0.3402	0.8705	0.088
H(11B)	4*a*	0.47	0.9262	0.3384	0.9535	0.088
C(11')	4*a*	0.53	0.893(2)	0.3350(5)	0.844(5)	0.20(2)
H(11C)	4*a*	0.53	0.8424	0.3348	0.7850	0.238
H(11D)	4*a*	0.53	0.8162	0.3404	0.8841	0.238
H(12A)	4*a*		0.9462	0.4140	0.8464	0.292
H(12B)	4*a*		1.0370	0.3713	0.7965	0.292
H(12C)	4*a*		1.0967	0.3892	0.8911	0.292
H(13A)	4*a*		0.7782	0.1635	0.9856	0.112
H(13B)	4*a*		0.6830	0.1613	0.8953	0.112
H(14A)	4*a*		0.8851	0.0817	0.9589	0.136
H(14B)	4*a*		0.7951	0.0797	0.8667	0.136
H(15A)	4*a*		0.6475	0.0788	1.0220	0.142
H(15B)	4*a*		0.5672	0.0699	0.9282	0.142
H(16A)	4*a*		0.5980	–0.0132	1.0007	0.244
H(16B)	4*a*		0.7742	–0.0045	1.0123	0.244
H(16C)	4*a*		0.6919	–0.0135	0.9190	0.244
H(17A)	4*a*		0.9903	0.1891	0.7665	0.128
H(17B)	4*a*		0.9334	0.1309	0.7861	0.128
H(18A)	4*a*		0.7389	0.2161	0.7370	0.155
H(18B)	4*a*		0.6890	0.1558	0.7495	0.155
H(19A)	4*a*		0.8621	0.1346	0.6389	0.227
H(19B)	4*a*		0.8547	0.1965	0.6173	0.227
C(20)	4*a*	0.48(4)	0.656(3)	0.157(1)	0.577(2)	0.14(2)
H(20A)	4*a*	0.48	0.6857	0.1432	0.5222	0.210
H(20B)	4*a*	0.48	0.6029	0.1906	0.5664	0.210
H(20C)	4*a*	0.48	0.5914	0.1313	0.6016	0.210
C(20')	4*a*	0.52	0.723(6)	0.113(1)	0.612(3)	0.22(2)
H(20D)	4*a*	0.52	0.7493	0.1030	0.5544	0.323
H(20E)	4*a*	0.52	0.6144	0.1163	0.6105	0.323
H(20F)	4*a*	0.52	0.7567	0.0849	0.6523	0.323
H(21A)	4*a*		1.1337	0.1880	0.8996	0.122
H(21B)	4*a*		1.0725	0.1298	0.9160	0.122
H(22A)	4*a*		1.0624	0.2148	1.0407	0.167
H(22B)	4*a*		1.0154	0.1543	1.0571	0.167
H(23A)	4*a*		1.3127	0.1935	1.0409	0.267
H(23B)	4*a*		1.2778	0.1328	1.0151	0.267
C(24)	4*a*	0.52(5)	1.263(5)	0.147(2)	1.147(2)	0.18(2)
H(24A)	4*a*	0.52	1.3672	0.1387	1.1654	0.274
H(24B)	4*a*	0.52	1.2014	0.1157	1.1556	0.274
H(24C)	4*a*	0.52	1.2300	0.1764	1.1814	0.274
C(24')	4*a*	0.48	1.387(6)	0.130(3)	1.087(6)	0.41(6)
H(24D)	4*a*	0.48	1.4777	0.1509	1.0819	0.608
H(24E)	4*a*	0.48	1.3926	0.0969	1.0553	0.608
H(24F)	4*a*	0.48	1.3786	0.1221	1.1477	0.608

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	4*a*	0.3179(2)	0.21239(6)	0.7285(1)	0.0675(6)	0.1114(9)	0.0785(7)	0.0130(8)	0.0160(6)	0.0127(8)
S(1)	4*a*	0.4902(6)	0.4899(2)	0.8056(3)	0.189(5)	0.122(3)	0.171(4)	0.002(3)	0.077(3)	–0.020(3)
S(2)	4*a*	0.4836(4)	0.3750(1)	0.8670(2)	0.100(2)	0.120(2)	0.123(2)	0.017(2)	0.013(2)	–0.009(2)
S(3)	4*a*	0.3403(5)	0.4019(1)	0.6990(2)	0.159(3)	0.115(2)	0.101(2)	0.027(2)	0.040(2)	0.016(2)
S(4)	4*a*	0.4196(4)	0.2549(1)	0.8428(2)	0.087(2)	0.114(2)	0.094(2)	0.021(2)	–0.004(2)	0.014(2)
S(5)	4*a*	0.2538(4)	0.2851(2)	0.6567(2)	0.123(3)	0.124(2)	0.074(2)	0.018(2)	0.010(2)	0.017(2)
S(6)	4*a*	0.3644(4)	0.1311(2)	0.7843(2)	0.086(2)	0.120(2)	0.089(2)	0.018(2)	0.002(2)	0.010(2)
S(7)	4*a*	0.2305(4)	0.1599(1)	0.6201(2)	0.104(2)	0.130(3)	0.086(2)	0.016(2)	0.009(2)	0.007(2)
C(4)	4*a*	0.298(1)	0.1060(6)	0.6850(7)	0.074(7)	0.13(1)	0.087(7)	0.008(7)	0.018(6)	0.009(7)
C(1)	4*a*	0.441(2)	0.4263(5)	0.7923(9)	0.12(1)	0.110(9)	0.15(1)	0.005(8)	0.072(9)	–0.018(7)
C(2)	4*a*	0.406(1)	0.3215(5)	0.8049(8)	0.050(5)	0.13(1)	0.097(8)	0.031(7)	0.015(5)	0.011(8)
C(3)	4*a*	0.336(2)	0.3323(4)	0.7256(9)	0.12(1)	0.085(7)	0.096(7)	0.024(7)	0.044(8)	0.022(7)
N(1)	4*a*	0.297(1)	0.0557(4)	0.6622(6)	0.115(6)	0.106(6)	0.101(6)	0.011(6)	0.001(5)	–0.017(5)
C(5)	4*a*	0.362(2)	0.0145(5)	0.7234(9)	0.13(1)	0.106(8)	0.120(9)	0.001(8)	0.01(1)	0.016(8)
C(6)	4*a*	0.523(2)	0.0033(7)	0.710(1)	0.16(2)	0.18(1)	0.17(1)	0.06(1)	0.03(1)	0.03(1)
C(7)	4*a*	0.243(2)	0.0401(6)	0.573(1)	0.18(2)	0.13(1)	0.15(1)	0.00(1)	–0.03(1)	0.01(1)
C(8)	4*a*	0.086(2)	0.0173(9)	0.569(1)	0.17(2)	0.22(2)	0.16(2)	–0.01(2)	0.01(1)	–0.02(1)
N(2)	4*a*	0.9032(9)	0.1840(3)	0.8849(5)	0.065(5)	0.102(6)	0.082(5)	0.004(5)	0.014(4)	–0.016(4)
C(9)	4*a*	0.864(1)	0.2410(5)	0.8976(7)	0.074(6)	0.111(8)	0.097(7)	0.011(6)	0.015(6)	–0.009(6)
C(10)	4*a*	0.972(2)	0.2802(4)	0.8624(9)	0.096(8)	0.105(8)	0.126(9)	0.024(7)	–0.006(8)	0.009(7)
C(12)	4*a*	1.008(2)	0.3819(6)	0.853(1)	0.19(2)	0.14(1)	0.25(2)	–0.01(1)	0.02(2)	–0.01(1)
C(13)	4*a*	0.780(1)	0.1516(5)	0.9256(6)	0.073(6)	0.13(1)	0.079(6)	–0.003(6)	0.020(5)	–0.014(6)
C(14)	4*a*	0.791(1)	0.0921(5)	0.9262(8)	0.096(8)	0.13(1)	0.118(8)	–0.024(8)	0.041(7)	–0.003(7)
C(15)	4*a*	0.660(1)	0.0633(6)	0.9652(8)	0.101(8)	0.17(1)	0.086(6)	–0.025(9)	0.003(6)	0.016(7)
C(16)	4*a*	0.683(2)	0.0024(6)	0.975(1)	0.19(2)	0.13(1)	0.18(1)	–0.03(1)	0.06(1)	0.01(1)
C(17)	4*a*	0.908(1)	0.1690(6)	0.7893(7)	0.100(9)	0.15(1)	0.076(6)	–0.018(8)	0.036(7)	–0.022(6)
C(18)	4*a*	0.770(2)	0.1787(7)	0.7321(7)	0.10(1)	0.21(1)	0.073(6)	–0.03(1)	0.021(7)	–0.020(8)
C(19)	4*a*	0.798(2)	0.1666(9)	0.639(1)	0.18(1)	0.21(1)	0.17(1)	–0.011(9)	0.025(9)	–0.010(9)
C(21)	4*a*	1.057(1)	0.1680(5)	0.9273(8)	0.066(6)	0.110(8)	0.13(1)	0.013(6)	0.008(6)	0.003(7)
C(22)	4*a*	1.082(2)	0.1773(7)	1.027(1)	0.086(9)	0.19(2)	0.14(1)	–0.01(1)	0.008(8)	0.04(1)
C(23)	4*a*	1.248(3)	0.163(1)	1.051(1)	0.17(2)	0.30(3)	0.19(2)	0.02(2)	–0.05(2)	0.06(2)

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