

Synthesis, crystal and molecular structure of bis(triethanolamine)nickel(II)dithiodisalicylate, [Ni(N(C₂H₄OH)₃)] [OOC C₆H₄SS C₆H₄COO]

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[Ni(N(C₂H₄OH)₃)₂] [OOC C₆H₄SS C₆H₄COO] / Nickel /
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Abstract. A Ni(II) complex involving triethanolamine (*tea*) and disulphide of thiosalicylic acid (*RSSR*) was synthesised and the crystal structure of the complex was solved. The molecular formula is C₂₆H₃₈N₂NiO₁₀S₂. The space group was found to be *I*2 with the following parameters $a = 27.872(2)$, $b = 9.016(2)$, $c = 27.820(2)$ Å, $\beta = 114.85(2)^\circ$, $V = 6343.8$ Å³, $Z = 8$, $D_x = 1.38$ g cm⁻³, $\mu = 0.739$ mm⁻¹. Final R was 0.102 and $R_w = 0.106$ for a total number of 2651 unique reflections with $I > 3 \sigma(I)$. Molecular structure of the complex showed an octahedral coordination around Ni(II) with a NiN₂O₄ chromophore inkeeping with the observed magnetic moment (3.1 BM). The average Ni–N and Ni–O distances are 2.16(3), 2.06(3) and 2.11(2), 2.06(2) Å respectively. One C₂H₄OH on each *tea* molecule is left uncoordinated. The disulphide moiety is acting as a counter ion and the average S–S distance is 2.077 Å. Eight molecules in the unit cell are held together by van der Waals forces.

Introduction

The interaction of metal ions with various mercaptocarboxylic acids have been investigated earlier (Kroneck et al., 1971). The mercaptocarboxylic

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acids have been extensively used as reagents in various analytical procedures. Ligands such as thiobenzoic acid and thiosalicylic acid provide both soft and hard donor centres and hence interesting coordination patterns in their complexes have been observed (Melson et al., 1970). Numerous complexation studies involving thiosalicylic acid have been carried out in the past (Subrahmanyam, 1982). But a survey of the literature shows that many of them are solution studies and the structure determinations are very sparse. Thiosalicylic acid gets oxidised to disulphide even in air. The disulphide-dithiosalicylic acid also provides donor centres such as carboxylate ions. The interaction of transition metal ions with disulphides have been investigated recently (Higashi et al., 1977). In the present investigation, an attempt was made to prepare Ni(II)-dithiodisalicylic acid complex in triethanolamine-triethanolamine hydrochloride (tea-teaHCl) buffer medium. The resulting complex was found to be Ni(tea)₂RSSR. In this paper the results of a crystal structure determination are presented.

Experimental

Preparation of crystals

Dithiosalicylic acid was prepared by the oxidation of thiosalicylic acid in the presence of Cu(II) salts. NiCl₂ · 6H₂O (3 mmols) was dissolved in tea-teaHCl buffer solution (25 ml) (25 mmols of tea – 25 mmols of teaHCl). The pH of the resultant solution was 8.2. The disulphide RSSR (1 mmol) was also dissolved in the buffer solution (25 ml). The ligand solution was poured into the solution containing nickel chloride. Pale blue fragile crystals appeared after a day. The crystals were washed with water, methanol and dried in air. Good crystals were chosen by an examination under the polarizing microscope.

The density of the crystal was found to be 1.3 g cm⁻³ by floatation technique. An Enraf-Nonius CAD4 diffractometer was employed for data collection. The cell constants were determined from least-squares analysis of 25- high-angle reflections. The intensity data were collected by ω -2 θ technique with $2 < \theta < 21^\circ$. Of the 4978 reflections, 2651 unique reflections with $I > 3 \sigma(I)$ were used for structure determination. The crystal data are given in the Abstract.

Determination of the structure

A careful examination of the observed data showed the absence of all ($h + k + l$) odd reflections. Based on this observation the space group was assumed to be *I*2 which was found to be correct later. The measured

intensities were corrected for background, attenuation and scan speed. Absorption and extinction corrections were not applied, μ being 0.739 mm^{-1} . Atomic scattering factors of Cromer (Cromer et al., 1968) and Stewart (Stewart et al., 1970) for non-H atoms and H atoms respectively were used.

The unit cell contained 8 mol and each asymmetric unit 2 mol. Two Ni atom positions 0.52, 0.25, 0.30 and 0.30, 0.0, 0.54 respectively were chosen from the Patterson map. A difference Fourier map with these two positions revealed the positions of other sulphur atoms and the residual was 0.45 at this stage. Later on all the 82 non-hydrogen atoms appeared in successive difference Fourier maps.

All the non-hydrogens were refined anisotropically. The four atoms O(14), C(25), C(30), C(44) showed very large movements. Moreover, due to the restriction on the number of atoms which can be refined anisotropically (SHELX-76), the aforesaid four atoms were only refined isotropically. Of the total 76 hydrogen atoms, 13 methylene hydrogens and 16 phenyl hydrogens were fixed geometrically. The hydroxyl hydrogens did not appear and the 35 hydrogens which appeared in the difference Fourier maps were refined isotropically. Standard deviations associated with the bonds reported in this structure are quite large. One of the reasons for this is the low ratio of the number of reflections to the parameters refined, the value being 3.5.

Discussion of the structure

The asymmetric unit in the unit cell contains 2 mol of $\text{Ni}(\text{tea})_2 \text{RSSR}$. The molecules are monomeric and the nickel complex is found to contain NiN_2O_4 chromophore in accordance with the observed paramagnetism of the complex. Fractional coordinates of all the non-hydrogens are listed in Table 1¹. The ORTEP plots (Johnson, 1976) of the molecules are shown in Figures 1 and 2. The packing of molecules in the unit cell is shown in Figure 3. The bond parameters of the 2 mol in one asymmetric unit differ only by the associated standard deviations.

Each nickel atom is in an octahedral environment of two nitrogens and four oxygens from two tea molecules. Two $-\text{CH}_2\text{CH}_2\text{OH}$ groups of each tea coordinate to the nickel ion and the third one does not. Relatively larger thermal parameters are observed for the uncoordinated oxygen atoms. The crystal structure of $\text{Ni}(\text{tea})_2(\text{NO}_3)_2$ has already been reported (Nielsen et al., 1972). The average Ni – N distances observed in the present compound

¹ List of the thermal parameters of non-hydrogen atoms, hydrogen atom positions with isotropic thermal parameters, bond lengths and angles and structure factors tables of this paper can be ordered referring to the no. CSD 52519, names of the authors and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 1. Positional parameters ($\times 10^4$) for non-hydrogen atoms with e.s.d.'s in parentheses.

	x	y	z		x	y	z
Ni(1)	531(2)	2500(0)	2985(2)	O(12)	1267(9)	2440(40)	5151(10)
N(1)	593(10)	4332(33)	2519(11)	O(13)	2021(7)	2036(23)	-1587(7)
C(1)	763(15)	5685(44)	2868(15)	O(14)	2830(8)	1989(25)	-948(8)
C(2)	1087(14)	5299(45)	3464(15)	C(25)	2226(11)	-533(35)	-2070(11)
O(1)	813(8)	4060(26)	3612(8)	C(26)	2414(13)	-1548(36)	-2356(11)
C(3)	974(14)	3851(44)	2331(14)	C(27)	2915(13)	-1627(46)	-2261(13)
C(4)	1478(13)	3154(43)	2740(12)	C(28)	3291(13)	-730(43)	-1901(12)
O(2)	1301(7)	2201(27)	3085(8)	C(29)	3159(10)	120(48)	-1560(12)
C(5)	68(14)	4648(48)	2109(14)	C(30)	2626(9)	396(32)	-1677(10)
C(6)	16(18)	5817(56)	1631(15)	C(31)	2457(13)	1610(35)	-1393(12)
O(3)	164(10)	4977(44)	1268(10)	S(1)	1567(3)	-326(9)	-2191(3)
N(2)	498(11)	722(34)	3444(10)	S(2)	1188(3)	-2230(10)	-2572(3)
C(7)	273(15)	-625(44)	3070(13)	C(32)	976(10)	-1835(35)	-3300(11)
C(8)	-43(14)	-50(47)	2490(14)	C(33)	1211(10)	-669(36)	-3410(11)
O(4)	282(9)	1017(26)	2359(8)	C(34)	1040(11)	-396(36)	-3969(12)
C(9)	119(14)	1298(51)	3672(14)	C(35)	637(12)	-1143(37)	-4344(13)
C(10)	-399(12)	1998(50)	3212(15)	C(36)	393(11)	-2416(40)	-4180(11)
O(5)	-244(8)	2967(24)	2903(8)	C(37)	592(12)	-2572(40)	-3631(11)
C(11)	1017(15)	451(45)	3871(14)	C(38)	317(11)	-3936(34)	-3486(14)

C(12)	964(20)	-1083(41)	4194(20)	O(15)	514(7)	-4427(25)	-3020(8)
O(6)	855(17)	-507(59)	4591(16)	O(16)	-93(8)	-4583(29)	-3833(8)
Ni(2)	2985(2)	-17(6)	5531(1)	O(17)	3410(8)	4524(23)	2025(8)
N(3)	3427(10)	-1780(32)	5483(10)	O(18)	4052(8)	4498(24)	2837(8)
C(13)	3071(13)	-3109(43)	5266(15)	C(39)	2931(10)	1955(34)	2230(11)
C(14)	2495(13)	-2573(44)	4968(12)	C(40)	2638(12)	932(35)	2407(13)
O(7)	2352(8)	-1504(24)	5270(8)	C(41)	2739(12)	834(43)	2899(12)
C(15)	3657(13)	-1226(42)	5106(12)	C(42)	3109(11)	1776(39)	3305(13)
C(16)	3214(15)	-517(47)	4598(14)	C(43)	3441(12)	2621(47)	3163(11)
O(8)	2900(8)	481(23)	4757(7)	C(44)	3320(10)	2899(33)	2623(10)
C(17)	3843(14)	-2201(45)	5992(13)	C(45)	3596(12)	4121(35)	2463(12)
C(18)	4210(18)	-365(38)	5991(15)	S(3)	2808(3)	2195(9)	1564(3)
O(9)	4599(14)	-2988(48)	5861(18)	S(4)	2432(3)	250(9)	1194(3)
N(4)	2509(11)	1828(31)	5582(10)	C(46)	1704(10)	654(32)	983(10)
C(19)	2324(12)	1363(40)	5981(13)	C(47)	1603(10)	1858(33)	1217(10)
C(20)	2755(12)	684(40)	6472(13)	C(48)	1035(12)	2111(41)	1043(11)
O(10)	3080(8)	-302(25)	6301(7)	C(49)	642(12)	1338(39)	628(13)
C(21)	2878(14)	3157(42)	5769(14)	C(50)	819(12)	143(37)	403(11)
C(22)	3467(15)	2714(48)	6114(15)	C(51)	1369(12)	-95(38)	588(12)
O(11)	3603(8)	1548(27)	5804(8)	C(52)	1504(13)	-1457(41)	304(12)
C(23)	2096(13)	2142(45)	5070(15)	O(19)	1980(8)	-1914(25)	513(8)
C(24)	1662(13)	3233(51)	5014(15)	O(20)	1157(9)	-2112(29)	-91(8)

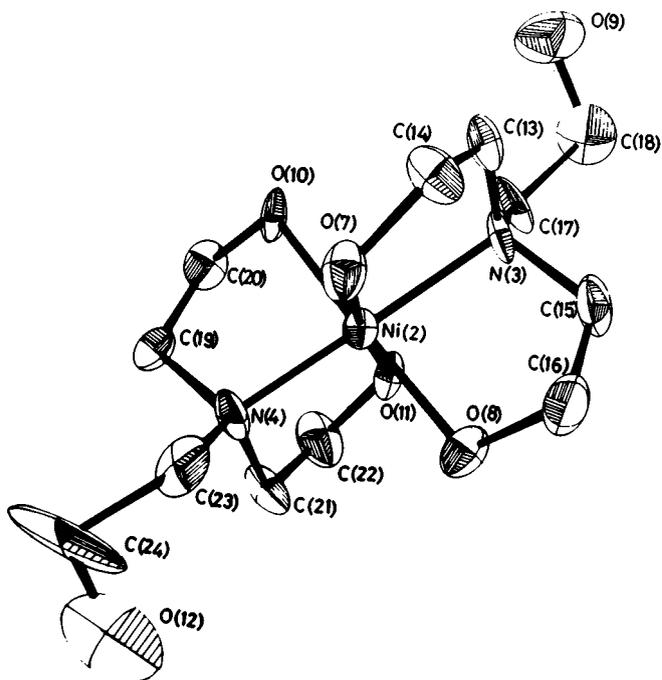


Fig. 1. ORTEP plot of $[\text{Ni}(\text{tea})_2]^{2+}$ cation.

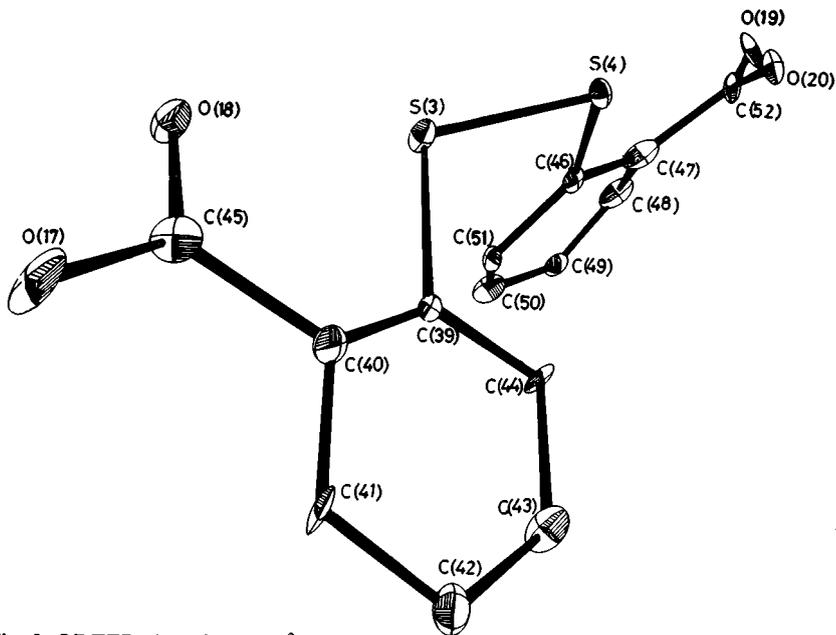


Fig. 2. ORTEP plot of $[\text{RSSR}]^{2-}$ anion.

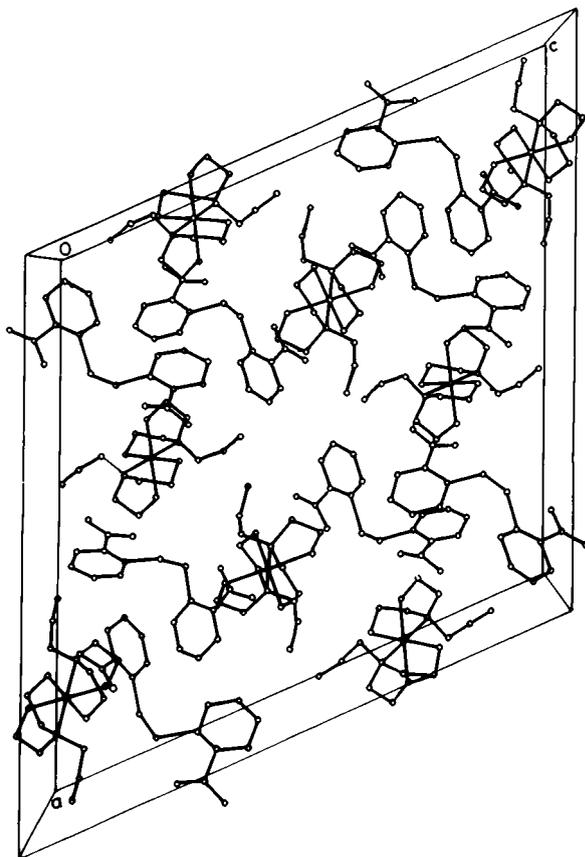


Fig. 3. Packing of $\text{Ni}(\text{tea})_2\text{RSSR}$ molecules in the unit cell.

of 2.16(3) and 2.06(3) Å agree with the reported value of 2.115(3) Å. Similarly, Ni–O distances average to 2.11(2) and 2.06(2) Å. In general Ni–N and Ni–O distances observed in this structure are in agreement with those observed in similar structure (Sacconi, 1968). In the present complex, the average normalized bite is 1.33° , which is defined as the distance between the effective bond centres divided by r , the average distance from the central atom (Kepert, 1982). The O–Ni–O angles lie in the range $63\text{--}65^\circ$ which are characteristic of the symmetric facial isomer as observed earlier (Nielsen et al., 1972).

The NiO_4 moiety is planar to within 0.01 Å. In the equatorial plane all the O–Ni–O angles are close to 90° . The N–Ni–N axis is not perpendicular to the plane of the oxygen atoms as the Ni–N bond is slightly inclined towards the direction of the chelated $\text{CH}_2\text{CH}_2\text{OH}$ moiety.

N—C—C—O is slightly puckered in such a way that the tetrahedral angles around carbon atoms are maintained and the octahedral coordination around Ni is also stabilised.

The dithiosalicylate ion acts as counter ion in the compound. The average S—S bond distance observed in the present complex, 2.07(1) Å, is close to those observed in similar compounds such as dibenzoyldisulphide (2.021(2) Å), tetraethylthiuramdisulphide (2.009(5) Å), 3,3'-dithiopropionic acid (2.033(4) Å) [Rout, 1984]. The phenyl rings are planar to within 0.02 Å. The phenyl rings of the disulphide unit are mutually perpendicular (interplanar angle is 90°). The bond distances involving C—C and C—O are normal.

The molecular packing in the unit cell is due to van der Waals forces. Intermolecular short contacts between the oxygens of the tea molecule and the carboxylate moieties are in the range 2.53 to 2.63 Å. This observation clearly shows the possibility of hydrogen bonded interactions, but the hydroxyl hydrogens could not be located.

In conclusion, the interaction of Ni(II) in tea-teaHCl buffer with RSSR results only in a $[\text{Ni}(\text{tea})_2]^{2+}$ complex and deprotonated RSSR acts as a counter ion.

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