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Reversible and Non-reversible Inclusion Compounds of the Nickel Xanthate Adducts with 4,4′-Bipyridyl and with 2,2′-Dipyridylamine

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Abstract

The crystal structures of the benzene inclusion compound of the 2,2′-dipyridylamine nickel ethylxanthate adduct, $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$, and the carbon tetrachloride inclusion compound of the 4,4′-bipyridyl nickel butylxanthate adduct, $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$, have been determined by single crystal X-ray diffraction methods.

Crystals of $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$ are triclinic, space group $P\bar{1}$, $a = 8.755(2)$, $b = 12.680(3)$, $c = 13.012(3)$ Å, and $\alpha = 110.12(2)$, $\beta = 106.09(2)$, $\gamma = 92.56(2)^\circ$ with $Z = 2$; R and Rw were 0.060 and 0.064 respectively for 3073 unique observed reflections. The nickel atom is in an octahedral environment, surrounded by two chelating xanthate ligands and one chelating 2,2′-dpa molecule. The benzene molecules sit in cavities formed by the packing of the $[Ni(S_2COEt)_2(2,2'\text{-dpa})]$ molecules, there being two benzene molecules in each cavity.

Crystals of $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$ are triclinic, space group $P\bar{1}$, $a = 6.6349(8)$, $b = 11.3135(9)$, $c = 13.1101(9)$ Å, α 64.454(7), $\beta = 79.551(8)$, $\gamma = 84.984(8)^\circ$, $Z = 2$; R and Rw were 0.040 and 0.044 respectively for 3018 unique reflections. The nickel atom is in an octahedral environment which results from two chelating xanthate ligands and two nitrogen atoms, one from each of two 4,4′-bipyridyl ligands. The nitrogen atoms are in a *trans* configuration which gives rise to a linear polymer of composition $[Ni(S_2COBu)_2(4,4\ \text{-bipy})]_n$. The CCl_4 molecules sit in open channels, parallel to the a-axis, which are formed by the packing of the linear polymeric chains of the complex.

Introduction

It has been observed [1–3] that adducts of heterocyclic diamines with nickel xanthates are capable of occluding solvent molecules. Two types of behaviour have been identified, *viz.* one where the occluded solvent could not be removed without destroying the crystal and the other where the solvent could be adsorbed and desorbed without changing the crystalline form of the adduct. The differences in the interactions between the host and guest molecules for the two types has remained speculative even though the adsorption and desorption processes have been studied in some detail [2, 3].

Crystals suitable for X-ray crystallography were obtained for the benzene inclusion compound of the 2,2′-dipyridylamine nickel ethylxanthate adduct $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6)]$, which represents the non-reversible type, and for the carbon tetrachloride inclusion compound of the 4,4′-bipyridyl adduct of nickel butylxanthate $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$, which is an example of the reversible type. Single crystal X-ray analyses have been undertaken in the hope of establishing the reason for the difference in the absorption/desorption behaviour of the nickel xanthate adducts.

Experimental

Green, needle shaped crystals of $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$ were obtained by adding $Ni(S_2COEt)_2$ (300 mg) dissolved in benzene (50 ml) to 2,2′-dipyridylamine (170 mg) dissolved in benzene (10 ml) and allowing the solution to stand for several hours. The crystals were stable and their chemical analysis confirmed the presence of one mole equivalent of benzene incorporated in the crystals. A well formed crystal was selected and cut to half its length giving a fragment of approximate dimensions 0.61 × 0.05 × 0.17 mm.

Long, brown crystals of $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$ were obtained by adding $Ni(S_2COBu)_2$ (350 mg) dissolved in hot CCl_4 (70 ml) to 4,4′-bipyridyl (150 ml) dissolved in hot CCl_4 (30 ml) and allowing the resultant solution to slowly cool. Crystals taken out of the mother liquor gradually changed colour (1–2 hours) indicating loss of CCl_4 and therefore manipulation was performed while they were still immersed in the mother liquor. A crystal of approximate dimensions 0.75 × 0.20 × 0.15 mm was selected and mounted in a sealed

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Lindemann glass capillary tube in the presence of the mother liquor. Attempts to cut the crystals into smaller fragments resulted invariably in their fracture.

Data Collection

Details of the data collection refer to $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$ with the corresponding details for $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$ in brackets.

Oscillation and Weissenberg photographs using Cu-Kα (nickel filtered) radiation showed that the crystals of both compounds were triclinic [4a]. The crystals were then mounted on an Enraf-Nonius CAD-4F single crystal automatic diffractometer. Accurate cell dimensions were obtained, by a least squares procedure, from the setting angles of 25 reflections measured using Mo-K$\bar{\alpha}$ (graphite monochromatized) radiation (λ = 0.71069 Å); 6 (15) reflections had a 2θ value greater than 38°. Intensity data were collected using the ω:2θ scan method to a maximum Bragg angle of 26° (27.5°) using Mo-K$\bar{\alpha}$ radiation: 6778 (5033) reflections were measured. Three reflections which were monitored every 1200 (2400) seconds of X-ray exposure time indicated that there was an approximately 6% (9%) decrease in intensity during the data collection and the intensity data were corrected in accordance with this variation; corrections were also made for Lorentz, polarisation and absorption effects [4b]. No corrections were made for extinction. Amalgamation of equivalent reflections and the application of the rejection criterion $I < 2\sigma(I)$ yielded 3073 (3018) unique observed reflections. Each of the crystals was well formed and the indices of the crystal faces for $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$ were ±(100), ±(01$\bar{1}$), ±(001) and for $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$ ±(100), ±(010) and ±(001). There was no apparent physical deterioration of either crystal during the data collection.

Crystal Data

$[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$

$C_{22}H_{25}N_3NiO_2S_4$, M = 550.4, light green needles, triclinic, a = 8.755(2), b = 12.680(3), c = 13.012(3) Å, α = 110.12(2), β = 106.09(2), γ = 92.56(2)°, U = 1301.92 Å^3, D_m (flotation) = 1.44 Mg m^{-3}, Z = 2, D_c = 1.420 Mg m^{-3}, $F(000)$ = 572, space group $P1$ (C_i^1, No. 2), Mo-K$\bar{\alpha}$ (graphite monochromated) λ = 0.71069 Å, μ = 1.091 mm^{-1}, absorption corrections applied.

$[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$

$C_{22}H_{26}Cl_8N_2NiO_2S_4$, M = 821.0, brown needles, triclinic, a = 6.6349(8), b = 11.3135(9), c = 13.1101(9) Å, α = 64.454(7), β = 79.551(8), γ = 84.984(8)°, U = 869.82 Å^3, D_m (flotation) = 1.56 Mg m^{-3}, Z = 1, D_c = 1.567 Mg m^{-3}, $F(000)$ = 416, space group $P\bar{1}$ (C_i^1, No. 2). Mo-K$\bar{\alpha}$ (graphite monochromated) λ = 0.71069 Å, μ = 1.361 mm^{-1}, absorption corrections applied.

Structure Determination

$[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$

The structure was solved from an E-map generated with the use of the SHELX-76 program system [5] from which the coordinates of the atoms of the 2,2'-dpa molecule, one xanthate ligand, and the nickel atom were assigned. The remaining non-hydrogen atoms were located from subsequent difference maps. Full matrix least squares refinement with individual anisotropic temperature factors converged with R 0.087, where $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. At this point it was noticed that the temperature factors of the carbon atoms of the two ethyl groups and the benzene molecule were rather high. A difference map calculated with these atoms removed (R 0.16) showed no evidence of disorder for any of these ten atoms. Refinement was continued with a weighting scheme of $w = 0.5713/(\sigma^2(F) + 0.0017\ F^2)$ and at convergence R and Rw were 0.067 and 0.072 respectively where $Rw = [\Sigma w \| F_o | - | F_c \|^2 / \Sigma w | F_o |^2]^{1/2}$. From the subsequent difference map peaks were found at positions attributable to all the hydrogen atoms of the 2,2'-dpa molecule as well as those of one of the xanthate ligands. For the other xanthate only three hydrogen atoms could be found. In addition there were weak peaks around the benzene molecule at positions suggestive of hydrogen atoms. The coordinates of the amine hydrogen atoms were refined but the positions of all the other hydrogen atoms, including those not evident in the difference map, were constrained at their geometrically estimated positions based on a C–H bond length of 1.08 Å. Refinement was continued until the maximum shift/e.s.d. was less than 0.05; the refinement converged with R 0.060 and Rw 0.064. The maximum peak in the final difference map was less than 0.65 eÅ^{-3}. The final atomic coordinates are presented in Table I.

$[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$

E-statistics suggested that the space group was centrosymmetric and as there is only one nickel atom per unit cell the nickel atom must be situated at a centre of symmetry. It was also noted that the b-axial length of approximately 11.3 Å would be close to that expected for the distance between metal atoms in the linear system Ni-4,4'-bipy-Ni, suggesting that the 4,4'-bipyridyl molecule was situated about the b-axis. The nickel atom was placed at the origin and the positions of the remaining non-hydrogen atoms were found from the subsequent difference maps. Full matrix least squares refinement with individual anisotropic temperature factors assigned

TABLE I. Atomic Coordinates of $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$; e.s.d. values are given in parentheses.

Atom	*x/a*	*y/b*	*z/c*
Ni	0.1859(1)	0.2359(1)	0.6428(1)
S(1)	0.2706(2)	0.0977(1)	0.7278(1)
S(2)	0.1356(2)	0.2980(1)	0.8349(1)
C(1)	0.2055(7)	0.1766(5)	0.8352(5)
O(1)	0.2134(7)	0.1363(4)	0.9176(4)
C(2)	0.1533(13)	0.1951(8)	1.0114(7)
C(3)	0.2019(21)	0.1422(13)	1.0949(11)
S(3)	0.0465(2)	0.3718(1)	0.5735(2)
S(4)	−0.1038(2)	0.1546(1)	0.5583(1)
C(4)	−0.1183(7)	0.2769(5)	0.5335(5)
O(2)	−0.2668(5)	0.2903(4)	0.4830(4)
C(5)	−0.2889(10)	0.3963(7)	0.4630(8)
C(6)	−0.4618(14)	0.3773(11)	0.3895(11)
C(7)	0.4280(8)	0.4400(5)	0.7965(6)
C(8)	0.5728(9)	0.5033(6)	0.8643(6)
C(9)	0.7086(9)	0.4600(6)	0.8461(6)
C(10)	0.6956(8)	0.3570(6)	0.7603(5)
C(11)	0.5418(7)	0.2992(5)	0.6933(5)
N(1)	0.4089(6)	0.3370(4)	0.7120(4)
N(2)	0.5279(6)	0.1967(4)	0.6044(4)
N(3)	0.2507(6)	0.1548(4)	0.4966(4)
C(12)	0.4044(7)	0.1431(5)	0.5024(5)
C(13)	0.4457(8)	0.0737(5)	0.4074(5)
C(14)	0.3266(9)	0.0169(6)	0.3046(5)
C(15)	0.1686(8)	0.0336(6)	0.2981(5)
C(16)	0.1387(7)	0.1016(5)	0.3950(5)
C(17)	0.7951(20)	0.3326(12)	0.0743(14)
C(18)	0.6790(17)	0.2465(16)	0.0075(10)
C(19)	0.6487(19)	0.1653(12)	0.0434(18)
C(20)	0.7389(33)	0.1639(17)	0.1501(25)
C(21)	0.8641(22)	0.2560(20)	0.2124(11)
C(22)	0.8880(17)	0.3387(11)	0.1764(13)

to the atoms converged with *R* 0.050. From the subsequent difference map it was observed that none of the carbon atoms in the butyl chain showed any sign of disorder and there was evidence of possible sites for all the hydrogen atoms. The refinement was continued with the hydrogen atoms constrained to their geometrically estimated positions with the C–H bond length fixed at 1.08 Å and with the application of the weighting scheme $w = 1.2202/(\sigma^2(F) + 0.00030\ F^2)$ until maximum shift/e.s.d. was less than 0.05; the refinement converged with *R* 0.040 and *Rw* 0.044. The final difference map revealed peaks of residual electron density close to the nickel, sulphur and oxygen atoms of less than 0.6 e $Å^{-3}$ together with peaks of approximately 0.7 e $Å^{-3}$ around the CCl_4 molecule which is suggestive of slight disorder for this molecule. Final atomic coordinates are given in Table II.

TABLE II. Atomic Coordinates of $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$; e.s.d. values are given in parentheses.

Atom	*x/a*	*y/b*	*z/c*
Ni	0.0000(–)	0.0000(–)	0.0000(–)
S(1)	0.2908(1)	−0.0725(1)	0.1051(1)
S(2)	−0.1465(1)	−0.0911(1)	0.2029(1)
C(1)	0.1019(4)	−0.1235(3)	0.2197(2)
O	0.1361(3)	−0.1893(2)	0.3268(2)
C(2)	0.3457(5)	−0.2253(4)	0.3473(3)
C(3)	0.3384(6)	−0.2996(4)	0.4732(3)
C(4)	0.2180(7)	−0.4248(4)	0.5257(4)
C(5)	0.2167(9)	−0.5018(5)	0.6534(4)
C(6)	−0.0015(4)	−0.4340(2)	0.0008(2)
C(7)	0.1749(5)	−0.3595(3)	−0.0368(3)
C(8)	0.1664(5)	−0.2380(3)	−0.0346(3)
N(1)	−0.0033(4)	−0.1869(2)	0.0018(2)
C(9)	−0.1732(5)	−0.2572(2)	0.0377(3)
C(10)	−0.1779(5)	−0.3805(3)	0.0386(3)
Cl(1)	0.8013(2)	−0.1631(1)	0.5229(1)
Cl(2)	0.9017(3)	−0.1441(2)	0.7172(1)
Cl(3)	0.4853(2)	−0.1218(2)	0.6829(1)
Cl(4)	0.6911(2)	−0.3692(1)	0.7453(1)
C(11)	0.7183(6)	−0.1981(4)	0.6661(3)

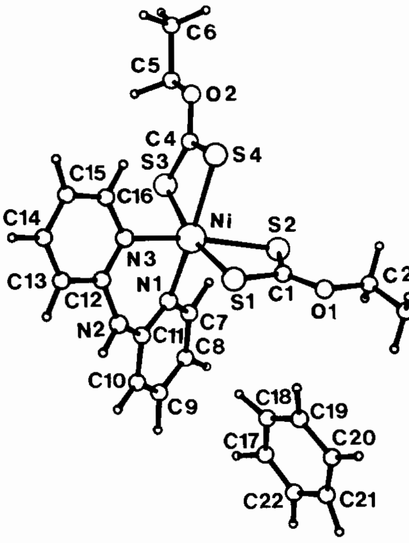

Fig. 1. Diagram of $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$ showing the labelling scheme; the benzene molecule is related by (x, y, 1 + z) to the coordinates given in Table I. Arbitrary thermal parameters have been assigned for reasons of clarity.

For both crystals the SHELX-76 program system [5] was used. The scattering factors for atomic H, C, N, O, S and Cl were those incorporated in the program while that for atomic Ni was that given in ref. [4c], the values being corrected for both the real and imaginary anomalous term [4d].

Listings of anisotropic temperature factors, estimated hydrogen atom positions, equations of mean planes, intermolecular contact distances and final observed and calculated structure factors for both compounds have been deposited with the Editors.

TABLE IIIa. Interatomic Distances (A) for [$Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6$]; e.s.d. values are given in parentheses.

Atoms	Separation	Atoms	Separation
Ni–S(1)	2.416(2)	S(3)–C(4)	1.673(6)
Ni–S(2)	2.520(2)	S(4)–C(4)	1.692(6)
Ni–S(3)	2.433(2)	C(4)–O(2)	1.332(7)
Ni–S(4)	2.479(2)	O(2)–C(5)	1.466(9)
Ni–N(1)	2.067(5)	C(5)–C(6)	1.507(15)
Ni–N(3)	2.074(5)		
		N(1)–C(7)	1.354(8)
S(1)···S(2)	2.922(2)	C(7)–C(8)	1.353(10)
S(1)···S(4)	3.664(2)	C(8)–C(9)	1.377(11)
S(1)···N(1)	3.310(5)	C(9)–C(10)	1.371(10)
S(1)···N(3)	3.290(5)	C(10)–C(11)	1.390(9)
S(2)···S(3)	3.720(2)	C(11)–N(1)	1.330(8)
S(2)···S(4)	3.410(2)	C(11)–N(2)	1.384(8)
S(2)···N(1)	3.330(5)	N(2)–C(12)	1.382(8)
S(3)···S(4)	2.918(2)	C(12)–N(3)	1.345(8)
S(3)···N(1)	3.318(5)	C(12)–C(13)	1.400(8)
S(3)···N(3)	3.362(5)	C(13)–C(14)	1.376(9)
S(4)···N(3)	3.415(5)	C(14)–C(15)	1.393(10)
N(1)···N(3)	2.867(7)	C(15)–C(16)	1.363(9)
		C(16)–N(3)	1.332(8)
S(1)–C(1)	1.676(6)	C(17)–C(18)	1.319(22)
S(2)–C(1)	1.683(6)	C(18)–C(19)	1.313(23)
C(1)–O(1)	1.325(8)	C(19)–C(20)	1.401(34)
O(1)–C(2)	1.445(11)	C(20)–C(21)	1.402(32)
C(2)–C(3)	1.443(17)	C(21)–C(22)	1.317(27)
		C(22)–C(17)	1.326(22)

TABLE IIIb. Bond Angles (°) for [$Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6$]; e.s.d. values given in parentheses.

Atoms	Angles	Atoms	Angles
S(1)–Ni–S(2)	72.55(5)	Ni–N(1)–C(11)	123.3(4)
S(3)–Ni–S(4)	72.88(5)	Ni–N(1)–C(7)	118.6(4)
N(1)–Ni–N(3)	87.61(19)	Ni–N(3)–C(12)	121.7(4)
S(1)–Ni–S(3)	166.42(7)	Ni–N(3)–C(16)	120.6(4)
S(1)–Ni–S(4)	96.92(6)	N(1)–C(7)–C(8)	123.9(6)
S(1)–Ni–N(1)	94.83(14)	C(7)–C(8)–C(9)	117.9(6)
S(1)–Ni–N(3)	93.90(14)	C(8)–C(9)–C(10)	120.4(7)
S(2)–Ni–S(3)	97.36(7)	C(9)–C(10)–C(11)	117.7(6)
S(2)–Ni–S(4)	86.03(5)	C(10)–C(11)–N(1)	123.1(6)
S(2)–Ni–N(1)	92.55(14)	C(11)–N(1)–C(7)	116.9(5)
S(2)–Ni–N(3)	166.42(15)	C(10)–C(11)–N(2)	117.9(5)
S(3)–Ni–N(1)	94.67(14)	N(1)–C(11)–N(2)	119.0(5)
S(3)–Ni–N(3)	96.16(15)	C(11)–N(2)–C(12)	129.9(5)
S(4)–Ni–N(1)	167.14(15)	N(2)–C(12)–C(13)	117.3(5)
S(4)–Ni–N(3)	96.76(15)	N(2)–C(12)–N(3)	120.9(5)
		N(3)–C(12)–C(13)	121.8(5)
Ni–S(1)–C(1)	84.9(2)	C(12)–C(13)–C(14)	119.4(6)
Ni–S(2)–C(1)	81.5(2)	C(13)–C(14)–C(15)	118.3(6)
S(1)–C(1)–S(2)	120.9(4)	C(14)–C(15)–C(16)	118.5(6)
S(1)–C(1)–O(1)	115.4(4)	C(15)–C(16)–N(3)	124.6(6)
S(2)–C(1)–O(1)	123.8(5)	C(16)–N(3)–C(12)	117.3(5)
C(1)–O(1)–C(2)	119.7(6)		
O(1)–C(2)–C(3)	106.4(9)	C(17)–C(18)–C(19)	119.9(1.4)
		C(18)–C(19)–C(20)	122.5(1.6)

(continued on facing page)

TABLE IIIb. *(continued)*

Atoms	Angles	Atoms	Angles
Ni-S(3)-C(4)	84.4(2)	C(19)–C(20)–C(21)	113.3(1.7)
Ni-S(4)-C(4)	82.5(2)	C(20)–C(21)–C(22)	122.9(1.6)
S(3)-C(4)-S(4)	120.2(4)	C(21)–C(22)–C(17)	119.1(1.4)
S(3)-C(4)-O(2)	124.5(5)	C(22)–C(17)–C(18)	122.2(1.4)
S(4)-C(4)-O(2)	115.3(4)		
C(4)-0(2)-C(5)	118.1(5)		
O(2)-C(5)-C(6)	104.9(7)		

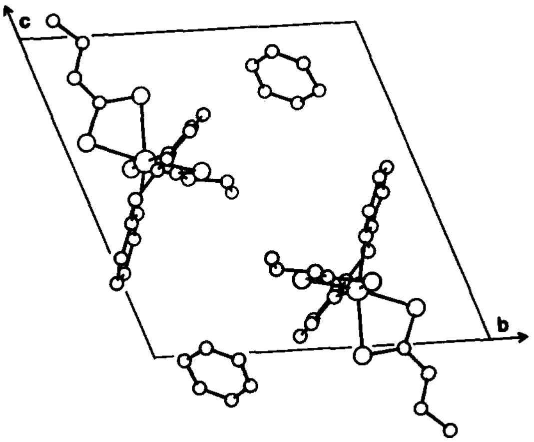

Fig. 2. The unit cell of [$Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6$] viewed normal to the bc-plane.

Results

Description of [$Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6$]

The molecular geometry and the numbering scheme used is shown in Fig. 1 while a view of the unit cell normal to the bc-plane is shown in Fig. 2. The nickel atom is in a distorted octahedral environment surrounded by two chelating xanthate anions and one chelating 2,2′-dpa ligand. Bond lengths and angles are given in Table III(a) and (b). The 2,2′-dpa molecule coordinates symmetrically to the nickel atom but there is slight asymmetry in the coordination of the two xanthate ligands. The Ni-S distances ***tram*** to the nitrogen atoms are greater than those ***trans*** to the sulphur atoms. The separation of 3.2 Å between the nickel and N(2) indicates that there is little interaction between these atoms.

The interaction of nickel(R) xanthate with the amine has resulted in increased values for the S-C-S angles and the M-S and C-O bond lengths; the values are similar to those found in the tris(xanthato)-nickelate(II) anion [6].

Both of the xanthate ligands are coplanar with the nickel atom, the greatest deviation being C(2) (0.107(11) Å) for ligand 1 and C(6) (0.095(13) A) for ligand 2. Interatomic contact distances between the [$Ni(S_2COEt)_2(2,2'\text{-dpa})$] molecules are those expected on the basis of the sum of the appropriate van der Waals radii [7].

The bond lengths and angles of the carbon atoms comprising the benzene molecule are normal, apart from those involving C(20); the angle of 113 is smaller than the expected value of 120°, while the two bond lengths are somewhat elongated. This could be a result of the movement of the benzene molecules in the cavity as is reflected in the high thermal parameters.

The Cavity

The benzene molecules lie in cavities formed by the packing of [$Ni(S_2COEt)_2(2,2'\text{-dpa})$] molecules. The inclusion compound is thus of the layer type [8]. In each cavity, which measures approximately 17 X 9 X 6 A, there are two benzene molecules, which are related by the centre of inversion (0, ½, 0). It is notable that the two benzene molecules are coplanar, the greatest deviation from the mean plane being 0.026(16) A for C(19). There are no noteworthy intermolecular contacts between the benzene molecules and the [$Ni(S_2COEt)_2(2,2'\text{-dpa})$] molecules.

Two views of the cavity are shown in Fig. 3a and 3b. The plots were drawn by the program ORTEP [9], using the 'box of enclosure' instructions. Apparent coordination anomalies in both diagrams are due to the fact that atoms which fall outside the box dimensions are excluded from the diagram, and hence the bonds to those atoms are also excluded. Figure 3a shows the view looking normal to the plane of the benzene molecules. The top layer (thick lines) encloses all atoms between 2 Å above and 2 Å below the benzene molecules. The lower layer (thin lines) includes atoms from 6 A to 2 A below the plane of the benzene molecules. The layer above the benzene molecules (not shown) would be the lower layer inverted through (0, ½, 0).

Figure 3b shows the view along the plane of the benzene molecules. The front layer (thick lines) extends from 2.7 Å in front of to 2.7 A behind (0, ½, 0) so that all the hydrogen atoms are included in this layer. The back layer (thin lines) extends

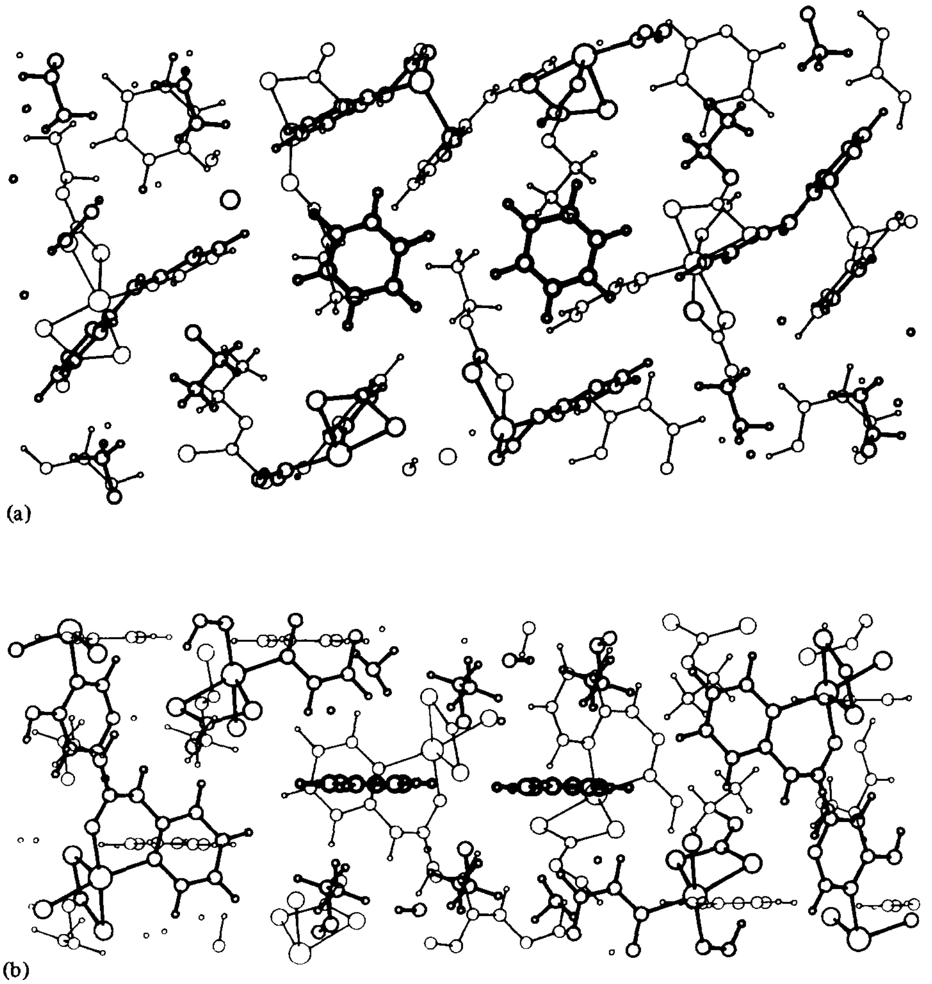

Fig. 3. The cavity of $[Ni(S_2COEt)_2(2,2'\text{-dpa})\cdot C_6H_6]$ viewed (a) normal to the plane of the benzene molecules; (b) along the plane of the benzene molecules which shows the discrete nature of the cavity in which the benzene molecules are imprisoned by the lattice of the host complex;other details are specified in the text.

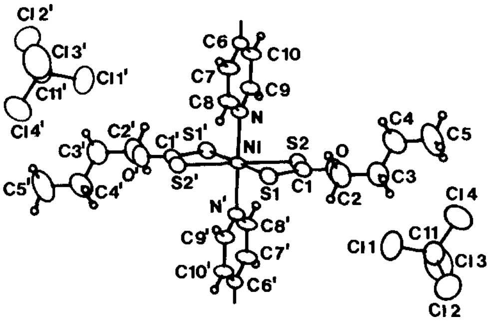

Fig. 4. Diagram of $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$ showing the labelling scheme.

from 2.7 Å to 8.0 Å behind (0, ½, 0). The layer in front (not shown) would be this layer inverted through (0, ½, 0).

Both diagrams show that the benzene molecules are completely enclosed in the cavities. Thus, it is likely that on crystallization the adduct molecules (host) arrange themselves around the benzene molecules (guest), completely surrounding them. Release of the benzene molecules can be achieved only by rupture of the structure.

Description of $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]$

The numbering scheme used for' this structure analysis is shown in Fig. 4 and Fig. 5 presents a packing diagram viewed down the a-direction. Bond lengths and angles are given in Table IV(a), and (b).

The nickel atom is in an octahedral environment resulting from four sulphur atoms, derived from two chelating xanthate anions, and two nitrogen atoms, one from each of two 4,4'-bipyridyl ligands with the nitrogen atoms in the ***tram*** configuration. This gives rise to a linear polymer, formed by the bridg-

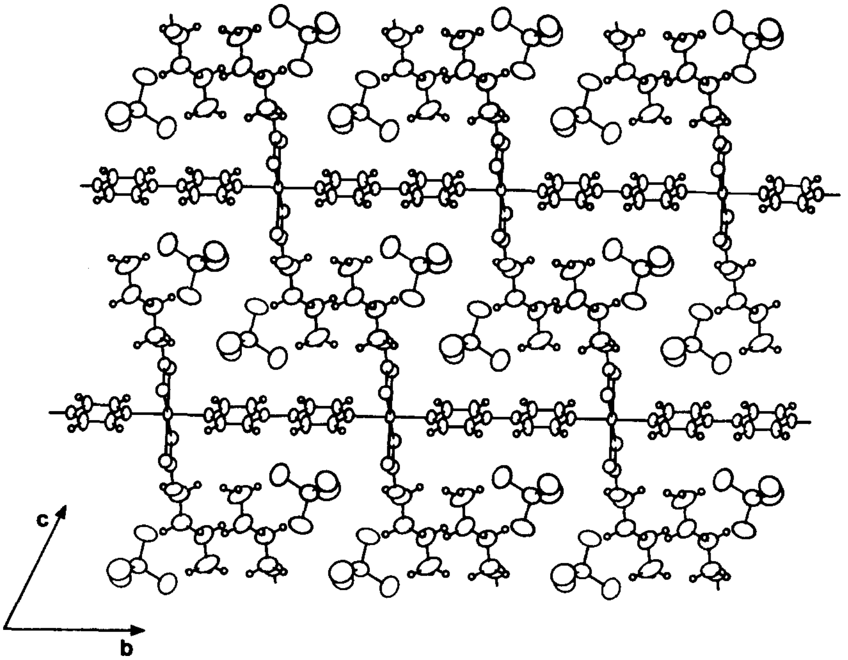

Fig. *5.* View of $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$ viewed along the a-axis *i.e.* looking down the channels with CC4 molecules.

TABLE IVa. Interatomic Distances (A) for $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$; e.s.d. values are given in parentheses.

Atoms	Separation	Atoms	Separation
Ni-S(1)	2.4505(9)	C(6)-C(7)	1.389(4)
Ni-S(2)	2.4407(11)	C(7)-C(8)	1.383(5)
Ni-N	2.106(3)	C(8)-N	1.326(4)
		N-C(9)	1.329(4)
S(l)* ••S(2)	2.938(1)	C(9)-C(10)	1.393(5)
S(1). ••S(2^I)^a	3.910(2)	C(lO)-C(6)	1.380(4)
S(1)•••N	3.199(3)	C(6)-C(6^{II})^b	1.501(4)
S(2)•••N	3.225(3)		
S(1)•••N^I ^{a}	3.264(3)	C(11)-Cl(l)	1.734(4)
S(2)•••N^I ^{a}	3.223(3)	C(11)-Cl(2)	1.756(5)
		C(11)-Cl(3)	1.729(5)
S(1)-C(1)	1.691(3)	C(11)-Cl(4)	1.766(5)
S(2)-C(1)	1.690(3)		
C(1)-O	1.327(3)	Cl(1)•••Cl(2)	2.845(2)
O-C(2)	1.454(4)	Cl(1)•••Cl(3)	2.845(2)
C(2)-C(3)	1.488(5)	Cl(1)•••Cl(4)	2.852(2)
C(3)-C(4)	1.509(7)	Cl(2)•••Cl(3)	2.851(2)
C(4)-C(5)	1.517(7)	Cl(2)•••Cl(4)	2.864(3)
		Cl(3)•••Cl(4)	2.851(3)

^{a}I: -x, -y, –z; ^{b}II: -x, 1 – y, -z.

TABLE IVb. Bond Angles (°) for $[Ni(S_2COBu)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$; e.s.d. values are given in parentheses.

Atoms	Angles	Atoms	Angles
S(l)-Ni-S(2)	73.84(3)	C(6)-C(7)-C(8)	119.5(3)
S(l)-Ni-S(l^{I})^{a}	180(–)	C(7)-C(8)-N	123.5(3)
S(l)-Ni-N' ^{a}	106.16(3)	C(8)-N-C(9)	117.6(3)
S(1)–Ni–N	88.83(8)	N-C(9)-C(10)	122.6(3)
S(1)–Ni–N^{a}	91.17(8)	C(9)-C(lO)-C(6)	120.0(3)
S(2)–Ni–S(2^{I})^{a}	180(–)	C(lO)-C(6)-C(7)	116.9(3)
S(Z)-Ni-N	90.05(7)	C(7)–C(6)–C(6^{II})^{b}	121.0(3)
S(1)–Ni–N$^{I\,a}$	89.95(7)	C(10)–C(6)–C(6)^{b}	122.1(3)
N-Ni-N' ^{a}	180(–)	C(8)-N-Ni	120.4(2)
		C(9)-N-Ni	122.0(2)
Ni-S(l)-C(1)	82.45(9)		
Ni-S(2)-C(1)	82.78(9)	Cl(1)–C(11)–Cl(2)	109.2(2)
S(l)-C(l)-S(2)	120.7(2)	Cl(1)–C(11)–Cl(3)	110.5(2)
S(1)–C(1)–O	123.4(2)	Cl(1)–C(11)–Cl(4)	109.2(3)
S(2)-C(l)-0	115.8(2)	Cl(2)–C(11)–Cl(3)	109.8(3)
C(l)-O-C(2)	118.8(2)	Cl(2)–C(11)–Cl(4)	108.9(2)
0-C(2)-C(3)	107.3(3)	Cl(3)–C(11)–Cl(4)	109.3(2)
C(2)-C(3)-C(4)	114.4(4)		
C(3)-C(4)-C(5)	114.0(4)		

^{a}I: -x, -y, –z. ^{b}II: -x, 1 – y, –z.

ing of $Ni(S_2COBu)_2$ units by 4,4'-bipyridyl ligands; the linear polymer chain lies along the b-axis.

The interaction of nickel(H) butylxanthate with the amine has also resulted in increased values for the S-C-S bond angle as well as an elongation of the C-O and Ni-S bond lengths and these values are comparable to those found for the tris(xanthato)-nickelate anion [6]. The S_2COC_2 atoms of both xanthate ligands together with the nickel atom are coplanar, the greatest deviation from the plane being 0.141(1) Å for S(1). The plane of the bipyridyl ligand (greatest deviation: C(6) 0.003(2) Å) which is essentially perpendicular to the $Ni(S_2COC_2)_2$ plane (dihedral angle 86.80°), bisects the S(1)–Ni–S(2^{I}) and S(2)–Ni–S(1^{I}) angles; I denotes an atom at the equivalent position (-x, –y, –z). There are no significant interactions between the polymeric chains.

The *Cavity*

The cavities that are formed by the packing of the $[Ni(S_2COBu)_2(4,4'\text{-bipy})]_n$ chains are channels which are directed parallel to the a-axis. Figure 5 shows a view of the structure along the a-axis *i.e.* looking down the channel. In each channel, which has a cross-section of approximately 12 X 6 Å, there are two columns of CCl_4 molecules which are related to each other through the centre of inversion (½, 0, ½). Atomic separations between the CCl_4 molecules and the $[Ni(S_2COBu)_2(4,4\text{-bipy})]_n$ chains are those expected from van der Waals radii of the atoms involved. The closest interactions are those between chlorine atoms and three of the hydrogen atoms on the butyl chain which have separations of approximately 3.0 Å comparing well with the sum of their van der Waals radii of 2.95 Å [7]. Movement of the CCl_4 molecule in the *b*- and c-axial directions is limited by the xanthate and the bipyridyl ligands respectively. In the a-direction there is, however, little restriction on the movement of the CCl_4 molecules in the channel. As the channel is open at both ends the CCl_4 molecules can easily move along the channel and escape at the crystal surface thereby accounting for the reversible nature of the adsorption/desorption behaviour found for this system.

Conclusion

By virtue of the proximity of the nitrogen atoms 2,2'-dpa acts as a chelating ligand forming isolated molecules of the adduct which on crystallization are arranged around and completely incapsulate two benzene molecules, so that the latter form an integral part of the crystal. In contrast, the position of the nitrogen atoms in 4,4'-bipy results in cross-linking to form infinite chains which are packed in such a way as to form open ended channels that accommodate the carbon tetrachloride molecules which can move freely.

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