Crystal Structure of Di-μ-tropolonato-bis[aquo(tropolonato)nickel(II)]

By **Roger J. Irving,* Michael L. Post, and David C. Povey,** Departments of Chemistry and Chemical Physics, University of Surrey, Guildford

Crystals of the title compound are monoclinic, $a = 9{\cdot}720(7)$, $b = 18{\cdot}888(17)$, $c = 7{\cdot}146(3)$ Å, $\beta = 97{\cdot}97(5)°$, $Z = 4$, space group $P2_1/n$. The structure was determined from diffractometer data by the heavy-atom method and refined by full-matrix least squares to R 0·082 for 1191 observed reflections. The molecule exists as a centrosymmetric dimer and contains two types of tropolone ligand: one co-ordinated to one nickel atom only, the other, co-ordinated both to the first nickel atom, and to a second nickel *via* a bridging oxygen atom. This, together with a co-ordinated water molecule gives the nickel atoms six-co-ordination. There is evidence for hydrogen bonding, *via* the water molecule, between adjacent dimers.

TROPOLONE displays the characteristic properties of a β-diketone in its ability to form a wide range of co-ordination compounds with transition metals.[1] Like acetylacetone, tropolone forms an anhydrous, presumably polymeric compound with nickel, $[\mathrm{NiT_2}]_n$ (T = tropolonate ion) but unlike $[\mathrm{Ni(acac)_2}]_3$ which reacts with water to give $\mathrm{Ni(acac)_2(H_2O)_2}$, $[\mathrm{NiT_2}]_n$ gives the unusual monohydrate $\mathrm{NiT_2(H_2O)}$, which is the subject of this investigation.

EXPERIMENTAL

Light green needle crystals were obtained from a solution of the compound (0·05 g) in methanol–water (100 ml, 3 : 1 v/v).

Crystal Data.—$\mathrm{C_{14}H_{12}NiO_5}$, $M = 318{\cdot}95$, Monoclinic, $a = 9{\cdot}720(7)$, $b = 18{\cdot}888(17)$, $c = 7{\cdot}146(3)$ Å, $\beta = 97{\cdot}97(5)°$, $U = 1299$ Å^3, $D_c = 1{\cdot}630$, $Z = 4$, $D_m = 1{\cdot}64$, (by flotation in aqueous zinc chloride), $F(000) = 688$, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 24$ cm^{-1}. Systematic absences; $0k0$ $k = 2n + 1$, $h0l$ $h + l = 2n + 1$. Space group, $P2_1/n$.

A crystal of dimensions 0·6 × 0·12 × 0·16 mm, parallel to a, b, and c respectively, was selected for the investigation. Unit-cell and space-group data were obtained from oscillation and Weissenberg photographs. The crystal was then mounted with the a axis parallel to the instrumental ϕ axis of a paper-tape controlled Siemens' four-circle diffractometer (A.E.D.) equipped with a scintillation counter and pulse-height discriminator. The unit-cell parameters were refined by a least-squares treatment of the θ values of 26 reflections. The intensities of 1993 symmetry-independent reflections $(\sin\theta)/\lambda \leqslant 0{\cdot}61$ were measured with Cu-K_α radiation by the θ—2θ technique, the scan ranges increasing linearly from 0·66° at θ 10° to 1·10° at θ 65°. The scan speed was 1° min^{-1} in θ and each reflection was scanned twice (one full and two half scans). The background was measured at both the beginning and end of each scan range for the same time as that for the full scan across the peak. A reference reflection (0,2,0) was monitored after every 20 data reflections. The intensity of this reflection decreased by 9% during the complete period of data collection. As a check on the long term stability of both electronics and crystal, a set of five reflections (0,1,1, $0,\bar{1},\bar{1}$, 0,7,2, $0,\bar{7},\bar{2}$, and 1,4,1) was measured every 250 data deflections. They showed no significant change, apart from the 9% decrease in intensity.

Integrated net intensities were calculated from the relationship: $I_{\text{net}} = [(I_1 + I_3 + I_5) - (I_2 + I_4)]$, where I_1 and I_3 are the intensities for the half-peak scans, I_5 is the intensity for the full-peak scan and I_2 and I_4 are the backgrounds at each end of the peak scan.

Each intensity was corrected for the variation of the reference reflection by the relationship

$$I_c = I_{\text{net}} \times I_R/[(I_a + I_b)/2]$$

where I_c is the corrected intensity, I_R is the intensity of the reference reflection at the start of the measurements and I_a, I_b are the intensities of the reference reflection at the beginning and end of each block of 20 reflections in which the measurement occurred. The intensities were assigned a variation of $\sigma^2(I)$, from the equation:

$$\sigma^2(I) = I_1 + I_2 + I_3 + I_4 + I_5$$

A reflection was classified as unobserved if $I/\sigma(I) \leqslant 2{\cdot}0$ and its intensity was replaced by $\sigma(I)$. Of the 1993 reflections, 802 were classified as unobserved. The intensities and their standard deviations were corrected for Lorentz and polarisation factors and placed on an approximately absolute scale by means of a Wilson plot. No absorption or extinction corrections were applied.

Structure Determination and Refinement.—The structure was determined by Fourier methods. A three-dimensional Patterson map gave the co-ordinates of the nickel atom and a structure factor calculation gave R 0·42. From an electron-density map phased on the nickel atoms, the remaining light atoms (excluding hydrogen) were found. A structure factor calculation on these atoms, including an overall isotropic temperature factor of B 4·5 Å^2, gave R 0·28.

Positional and isotropic thermal parameters and an overall scale factor all refined by full-matrix least squares decreased R to 0·18. At this point, a Cruickshank weighting scheme ($w^{-1} = A + B|F_o| + C|F_o{}^2|$, with $A = 6{\cdot}0$, $B = 1{\cdot}2$, and $C = 0{\cdot}004$) was applied to maintain the mean $w\Delta^2$ approximately constant for different ranges of F_o. Several more cycles of weighted least squares reduced R to 0·11 and introduction of anisotropic thermal parameters further reduced R to 0·086.

A three-dimensional difference-Fourier map revealed the positions of the hydrogen atoms. Two further cycles of least squares, including the hydrogen atoms, decreased R to its final value of 0·082. The hydrogen atoms were not refined and were allocated isotropic temperature factors of 5·0 Å^2.

Atomic scattering factors were taken from ref. 2. All calculations were performed on an Atlas computer of the S.R.C. Computing Laboratory, Harwell by use of the program system '*X*-Ray',[3] and as ICL 1905 F computer at the University of Surrey.

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[1] D. W. Thompson, *Structure and Bonding*, 1971, **9**, 27.

[2] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[3] '*X*-Ray '63,' program system, J. M. Stewart, University of Maryland Technical Report, TR 64 6.

Final positional and thermal parameters for all atoms excluding hydrogen are listed in Tables 1 and 2. Hydrogen positional parameters and their associated carbon–hydrogen bond lengths are listed in Table 3. Final observed and calculated structure factors are listed in supplementary publication No. SUP 20610 (11 pp., 1 microfiche).*

TABLE 1

Atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ni	5533(1)	4527(1)	6733(2)
O(1)	4825(7)	3667(3)	5154(9)
O(2)	4661(7)	3969(3)	8648(8)
O(3)	7512(8)	4149(4)	7132(9)
O(4)	6289(7)	4957(3)	4509(8)
O(5)	6038(7)	4589(4)	8125(8)
C(1)	4083(10)	3248(4)	5975(11)
C(2)	3940(10)	3430(4)	7945(11)
C(3)	3076(13)	3078(5)	9098(14)
C(4)	2182(12)	2499(5)	8713(15)
C(5)	1897(12)	2097(5)	7095(16)
C(6)	2491(11)	2171(5)	5454(16)
C(7)	3463(11)	2657(5)	4954(14)
C(8)	8137(12)	4222(5)	5713(14)
C(9)	7419(11)	4664(4)	4131(11)
C(10)	7801(11)	4747(5)	2351(14)
C(11)	9024(13)	4506(5)	1637(15)
C(12)	0152(13)	4134(6)	2521(17)
C(13)	0331(12)	3883(6)	4319(18)
C(14)	9480(13)	3919(6)	5741(16)

TABLE 2

Thermal parameters * in $[NiT_2(H_2O)]_2$: anisotropic parameters ($Å^2 \times 10$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	467	295	282	1	96	6
O(1)	458	213	217	−13	115	−41
O(2)	280	202	186	−11	106	1
O(3)	378	319	235	−41	62	23
O(4)	292	231	180	42	71	37
O(5)	380	265	250	−32	65	−48
C(1)	117	245	179	91	23	10
C(2)	222	183	206	97	53	44
C(3)	503	298	280	−111	105	43
C(4)	326	354	390	−78	99	9
C(5)	269	240	436	−27	52	−3
C(6)	200	292	475	−22	62	−85
C(7)	216	315	296	−26	59	−93
C(8)	295	231	264	−41	49	−3
C(9)	329	248	152	2	8	−31
C(10)	281	354	276	−30	147	−11
C(11)	365	461	330	−151	131	−21
C(12)	284	550	399	52	53	−12
C(13)	220	451	592	93	143	−43
C(14)	288	404	378	5	13	−32

* Temperature factors are in the form: $\exp -\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*$

TABLE 3

Atomic co-ordinates ($\times 10^3$) and bond lengths (Å) for the hydrogen atoms

Atom	*x*	*y*	*z*	H(*n*)–C(*n*)
H(3)	323	333	050	1·10
H(4)	175	222	968	1·01
H(5)	114	172	986	1·02
H(6)	200	194	436	0·96
H(7)	354	259	364	0·96
H(10)	707	496	132	1·03
H(11)	904	454	036	0·91
H(12)	061	437	109	1·25
H(13)	132	374	486	1·02
H(14)	968	369	691	0·94

DISCUSSION

A perspective drawing of the whole molecule, excluding hydrogen atoms, is shown in Figure 1. The molecule is dimeric, the centre of symmetry inherent in the space group lying midway between the two nickel atoms of each dimer.

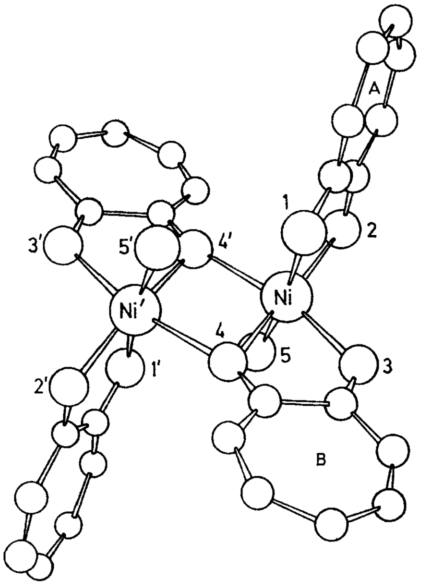

FIGURE 1 A perspective drawing of the dimer

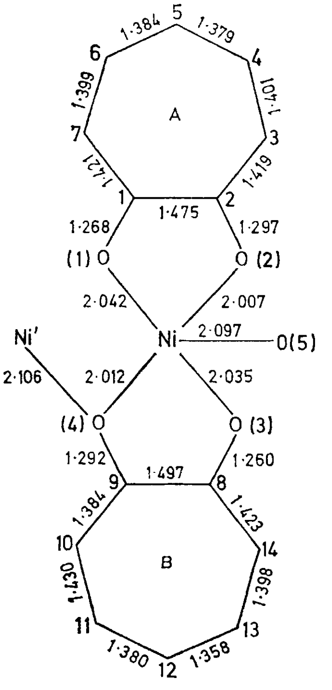

FIGURE 2 Bond distances (Å). Mean σ = Ni–Ni' 0·004, Ni–O 0·006, C–O 0·009, C–C 0·009 Å

Figures 1—3 show that there are two types of tropolone ligand in the complex: one (ligand A) co-ordinating to one nickel atom only and one (ligand B) which also co-ordinates to the first nickel atom and to the second *via* a bridging oxygen atom, O(4). With one ligand of

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

each type, and one water molecule, co-ordinated through O(5), to each nickel atom, a six-co-ordination is attained by the latter.

The bond lengths and ligand angles of the asymmetric unit of the complex are shown in Figures 2 and 3, together with the atom numbering scheme used. The nickel–nickel distance (3·11 Å) is too long for any metal–metal interaction to occur, and is longer than the corresponding distance in many other, associated, nickel complexes where the shorter Ni–Ni distance is structure determining. In tetrakis(2-aminoethanethiolato)trinickel(II),[4] bis(monothiobenzoato)nickel(II),[5] and bis-(dithiophenylacetato)nickel(II),[6] the Ni–Ni distances are 2·73, 2·49, and 2·56 Å. The possibility of dimer formation in the nickel tropolonate complex, to take advantage of metal–metal interaction can, therefore, be excluded.

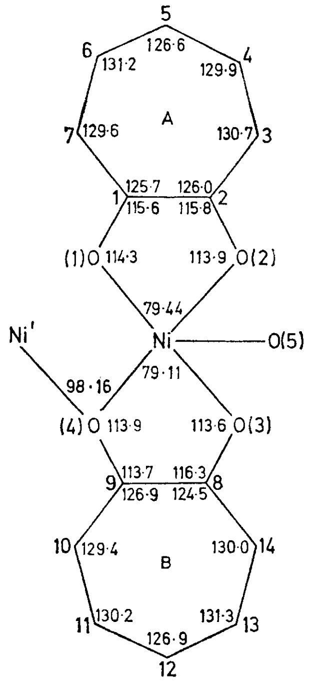

FIGURE 3 Bond angles (°). Mean σ = 0·2—0·9°

The nickel–oxygen distances exhibit a variation which appears to be real. The longer Ni–O(5) distance, for the co-ordinated water molecule indicates that it is not bonded as strongly to the nickel atom as are the tropolone molecules and this is in keeping with the chemical behaviour of the compound.

The atom O(4) forms bonds of unequal length to the two nickel atoms which it bridges. If one considers the steric requirements of the bridging tropolone ligand, the 'bite' of the ligand (the 'bite' is the distance between the chelating oxygen atoms of one ligand), does not exceed 2·60 Å in this structure, or in any of the published structures of tropolone compounds. From a geometrical consideration of the Ni–O distance (mean *ca.* 2·05 Å), and the angular relationships in the triangle formed by Ni–O(4)–Ni′, it is apparent that equal sharing of the bridging oxygen atom could only occur if the Ni–Ni′ distance was very much closer to 3 Å than it is in nickel tropolonate. It is incorrect to assume, therefore, that unequal sharing of the atom, O(4), is due to any inherent weakness of the tropolone ligand to form bridged complexes.

The carbon–carbon bond lengths are in good agreement with those reported for other tropolone complexes and with tropolone itself.[7] The mean carbon–carbon bond length is 1·401 Å for ring A, and 1·396 Å for ring B. The very much longer C(1)–C(2) and C(8)–C(9) distances, probably indicate that these bonds are not appreciably involved in the electron delocalisation experienced by the remainder of the ring. The mean C–H distance (1·04 Å) (Table 3) is in fair agreement with reported values.[8,9]

TABLE 4

Angles (°) subtended at the Ni^{II} atom

O(1)–Ni–O(2)	79·44 *	O(3)–Ni–O(4)	79·11 *
O(1)–Ni–O(3)	92·16	O(3)–Ni–O(5)	94·79
O(1)–Ni–O(4)	90·96	O(3)–Ni–O(4′)	160·86
O(1)–Ni–O(5)	171·98	O(4)–Ni–O(5)	86·43
O(1)–Ni–O(4′)	86·30	O(4)–Ni–O(4′)	81·84
O(2)–Ni–O(3)	101·55	O(5)–Ni–O(4′)	85·83
O(2)–Ni–O(4)	170·39	O(1)–Ni–Ni′	88·12
O(2)–Ni–O(5)	103·02	O(5)–Ni–Ni′	84·86
O(2)–Ni–O(4′)	96·92	Ni–O(4)–Ni′	98·16

* Angles subtended by the ligands.

TABLE 5

Oxygen–oxygen distances (Å) in the co-ordination polyhedron

O(1) · · · O(2)	2·588 *	O(2) · · · O(4′)	3·079 *
O(1) · · · O(3)	2·973	O(2) · · · O(5)	3·212
O(1) · · · O(4)	2·891	O(3) · · · O(4)	2·577 *
O(1) · · · O(4′)	2·838	O(3) · · · O(5)	3·041
O(1) · · · O(5)	2·862	O(4) · · · O(4′)	2·699
O(2) · · · O(3)	3·131	O(4) · · · O(5)	2·814

* Ligand 'bite' distances.

The co-ordination stereochemistry experienced by the nickel atom is considerably distorted octahedral. The primed numerals in Figure 1 denote the centrosymmetrically related atoms. The O–Ni–O angles are given in Table 4 and the oxygen–oxygen distances in the co-ordination polyhedron in Table 5. The angles subtended by the chelating oxygen atoms are *ca.* 79°, and this is due to the rigid co-ordination system of tropolone. Table 6 lists equations of best mean planes and deviations and atoms from these.

Both ligands A and B exhibit folding about the lines defined by the respective co-ordinating oxygen atoms. Thus, for ligand A, the plane defined by O(1), C(1), C(2), O(2) is at an angle of 8° to the plane O(1), Ni, O(2). For ligand B, the corresponding angle is 15°. In the

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[4] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 1970, **9**, 1878.

[5] N. Bonamico, G. Dessey, and V. Fares, *Chem. Comm.*, 1969, 697.

[6] N. Bonamico, G. Dessey, and V. Fares, *Chem. Comm.*, 1969, 1106.

[7] H. Shimanouchi and Y. Sasada, *Tetrahedron Letters*, 1970, **28**, 2421.

[8] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3626.

[9] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3636.

TABLE 6

Equations of test planes in the form $Px + Qy + Rz = S$ where x, y, and z are fractional co-ordinates. Deviations (Å) of atoms from the planes are given in square brackets

	P	Q	R	S
Plane (1): C(1)—(7), O(1), O(2)	−7·042	11·375	−1·655	−0·1663
[O(1) −0·087, O(2) 0·033, C(1) 0·004, C(2) 0·022, C(3) 0·004, C(4) −0·030, C(5) −0·040, C(6) 0·022, C(7) 0·071, Ni −0·305]				
Plane (2): C(1)—(7)	−6·909	11·506	−1·784	−0·1885
[C(1) −0·033, C(2) 0·005, C(3) 0·018, C(4) −0·001, C(5) −0·024, C(6) 0·008, C(7) 0·031, Ni −0·373]				
Plane (3): C(8)—(14), O(3), O(4)	4·158	15·698	2·089	11·2360
[O(3) 0·109, O(4) −0·103, C(8) 0·030, C(9) −0·033, C(10) 0·048, C(11) 0·067, C(12) −0·002, C(13) −0·058, C(14) −0·058, Ni 0·421]				
Plane (4): C(8)—(14)	4·054	15·985	1·932	11·2070
[C(8) 0·056, C(9) −0·053, C(10) 0·002, C(11) 0·030, C(12) −0·003, C(13) −0·022, C(14) −0·009, Ni 0·427]				

copper complex, CuT$_2$,[10] similar behaviour is reported although the angles concerned are only *ca.* 4°. CuT$_2$ was also found to exhibit carbon–carbon bond-length alternation around the ring, and this was thought to be due to the loss of ligand planarity, and a resulting decrease in electron delocalisation efficiency. No bond-length alternation is exhibited in the nickel complex or in the complexes ThT$_4$(DMF),[8] SnT$_3$Cl,[9] and SnT$_3$(OH),[9] where similar ligand-folding effects also exist.

The carbon rings also deviate from planarity. Ring A exhibits a fold with atoms C(2), C(3), C(6), and C(7) above the mean plane of the ring and atoms C(1), C(4), and C(5) below. Ring B exhibits a twist about an axis running through C(12) and the mid-point of C(8)–C(9).

The arrangement of adjacent molecules in the lattice, as viewed along the c axis, is shown in Figure 4, and as viewed along the a axis in Figure 5. Figure 4 shows how the tropolone rings of each molecule fit between the rings of adjacent molecules. The distance between adjacent molecules is not <3·7 Å, which is the mean distance for van der Waals interaction between aromatic rings.[11] Figure 5 shows that although the distance between neighbouring rings is not less than the van der Waals distance, atom O(5), of the water molecule, approaches parts of the adjacent molecule closely enough to indicate a much stronger interaction, which almost certainly indicates hydrogen bonding. Because the distance between O(5) and its nearest neighbour [O(2′) on the next molecule] is small (2·70 Å), the hydrogen bond is probably not linear. The appearance of the difference-Fourier synthesis in this region shows a toroid of electron density of *ca.* 0·5 eÅ^{-3}, surrounding the O(5) site. Unlike the ring hydrogen atoms, no definite hydrogen atom positions are apparent close to O(5). This may indicate greater thermal motion or disorder of the water molecule although the former is not supported by an increase in the thermal parameters for O(5). Each dimeric molecule has a strong interaction, through hydrogen bonding, to its

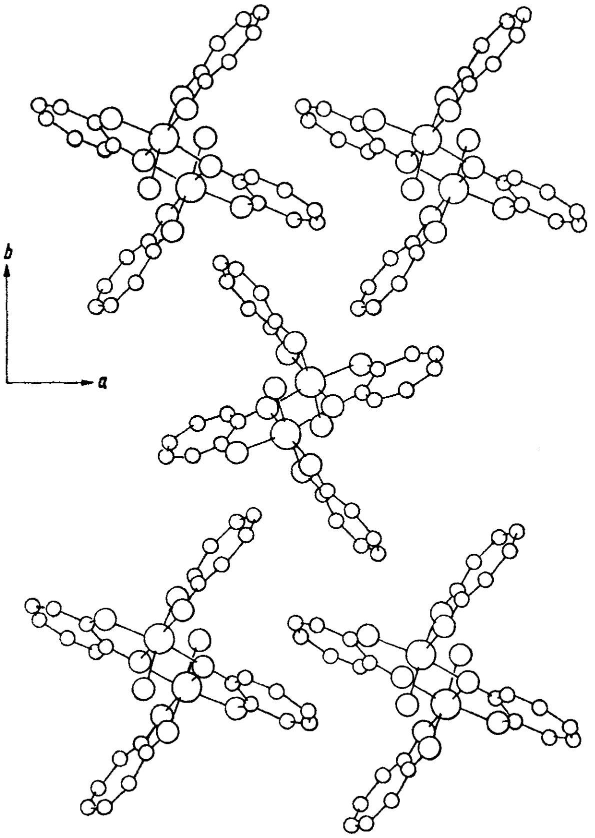

FIGURE 4 View along the c direction (five molecules), drawn on a left-handed system of axes viewed from $-c$

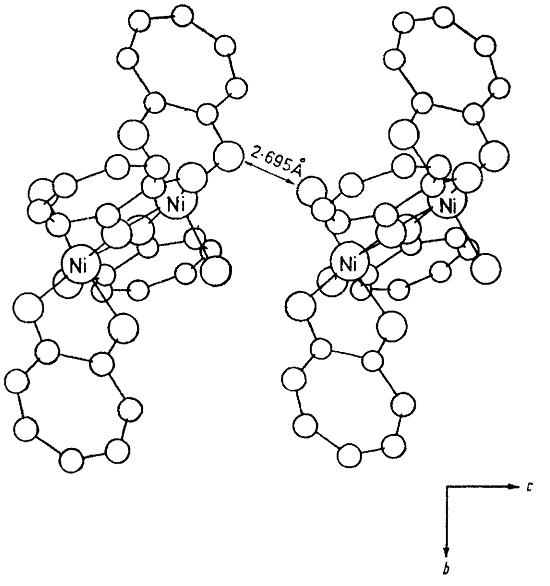

FIGURE 5 View along the a direction (two molecules)

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[10] W. M. McIntyre, J. M. Robertson, and R. F. Zahrobsky, *Proc. Roy. Soc.*, 1966, *A*, **289**, 161.

[11] R. C. Weast, 'Handbook of Chemistry and Physics,' 51st edn., Chemical Rubber Co., 1970.

neighbour and this results in lines of dimers along the *c* direction, so close together that they almost form a true polymeric lattice.

The reason for the stability of the present complex compared with bis(acetylacetonato)nickel(II) is probably connected with the ability of the tropolones of each dimer to approach adjacent molecules in the *c* direction sufficiently closely to allow the terminal water molecules to form hydrogen bonds with the closest tropolone oxygen atoms. Such an effect would be less likely if the ligands were not small and compact.

The present dimeric complex represents the first confirmed oxygen-bridged structure with tropolone. Other examples of bridge structures, such as the various seven-co-ordinate lanthanide complexes, almost certainly exist, and a preliminary study of the cobalt(II) complex with tropolone, shows it to be a tetramer.

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