Crystal Structure of $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$, the First Equidistant Stack d^7 Monoanion Metal Dithiolene Complex*

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The *X*-ray crystal structure of $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ has revealed that the planar $[Ni\{S_2C_2(CN)_2\}_2]^-$ anions form an eclipsed equidistant stack structure with a repeat distance of 3.918(8) Å. At 98 K the repeat distance in the stack direction is double that at room temperature indicating that the anions are now associated as dimers. The room-temperature structure and low-temperature transition are related to the unusual magnetic properties of this compound.

The study of metal dithiolenes has produced a rich variety of compounds with unusual structural and electronic properties. The discovery that metal dithiolene anions can form the conduction pathway for one-dimensional metallic behaviour has stimulated renewed interest in these compounds.[1] The non-integral oxidation state one-dimensional metal $Li_{0.82}(H_3O)_{0.33}[Pt\{S_2C_2(CN)_2\}_2]\cdot 1.67H_2O$ has been shown to possess a equidistant columnar stack structure with the anions arranged in an eclipsed configuration.[2] The interplanar separation is 3.592 Å. In contrast, the crystal structures of all the d^7 metal dithiolene monoanions of nickel and platinum determined so far possess a dimer structure, either with metal over metal (*e.g.* $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$) or metal over sulphur (*e.g.* $NEt_4[Ni\{S_2C_2(CN)_2\}_2]$) stacking.[3,4] The formation of a dimer as opposed to an equidistant stack structure has been attributed to the Peierls distortion associated with the formation of a half-filled band expected for these monoanions.

In 1980 Isett *et al.*[5] reported the preparation and properties of $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ and on the basis of the unit cell obtained from preliminary *X*-ray results proposed an equidistant stack structure for this compound. Unfortunately the quality of the crystals was not sufficient to allow the crystal structure to be determined. In the light of recent work this is a most important compound and following the same preparative route we have now obtained single crystals of a quality acceptable for *X*-ray study.

Experimental

The salt $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ was prepared by electrocrystallisation as previously described.[5,6]

Crystallography.—All *X*-ray measurements were made on a crystal of dimensions 0.8 × 0.15 × 0.1 mm, sealed inside a thin-walled glass capillary, using a CAD4 diffractometer with nickel-filtered Cu-K_α radiation (λ = 1.541 78 Å), operating in the ω—2θ scan mode as previously described in detail.[7] Detailed examination of the crystal showed rather variable and broad peak widths; as a result the cell dimensions are of a lower precision than normally obtained.

Crystal data. $C_8H_6N_5NiOS_4$, M = 365.1, orthorhombic, a = 12.096(4), b = 3.918(8), c = 29.216(5) Å, U = 1 384.8 Å^3, D_m = 1.793 g cm^{-3}, Z = 4, D_c = 1.799 g cm^{-3}, $F(000)$ = 756, $\mu(\text{Cu-}K_\alpha)$ = 73.55 cm^{-1}.

Table 1. Fractional atomic co-ordinates (× 10^4) for $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$

Atom	*x*	*y*	*z*
Ni	0	5 000	5 000
S(1)	803(1)	3 367(5)	4 381(0.5)
S(2)	−1 469(1)	6 607(5)	4 645(0.5)
C(1)	−168(4)	4 241(15)	3 973(2)
C(2)	−1 153(4)	5 709(16)	4 085(2)
C(10)	60(5)	3 373(18)	3 501(2)
N(10)	203(4)	2 662(17)	3 131(1)
C(20)	−1 947(5)	6 558(19)	3 736(2)
N(20)	−2 538(5)	7 273(20)	3 449(2)
O	−1 807(6)	2 075(24)	2 500
N(1)	−3 548(8)	7 187(25)	2 500

Intensity data were measured for one octant within the limits $3.0 \leqslant \theta \leqslant 60°$; of the 1 298 independent reflections measured, 745 were observed [$I > 1.5\sigma(I)$] and used for the analysis, after application of empirical absorption corrections.[8] The structure was solved and developed *via* the heavy-atom method and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically, hydrogens were located experimentally and included and refined isotropically, with N–H distances restrained to a value of 1.05 Å. This Ni atom is at a position of site symmetry $\bar{1}$, whilst the ammonium ions and water molecules lie on the mirror planes. The final values of R and R' were 0.042 and 0.039 respectively, with individual reflection weights of $w = 1/[\sigma^2(F_o) + 0.0002\ F_o^2]$. Atomic scattering factor data were taken from ref. 9 and all calculations were made on a VAX 11/750 computer using SHELX 76.[10] Final atomic positional parameters are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Description of the Room-temperature Structure.—Figure 1 shows the crystal structure as viewed down the *b* axis. Important interatomic distances and interbond angles are given in Table 2; the geometry parameters in the $[Ni\{S_2C_2(CN)_2\}_2]^-$ ion give average bond lengths Ni–S 2.152(3), S–C 1.713(10), 'C=C' 1.363(8), C–C 1.441(8), and C–N 1.134(7) Å.

The structure contains equidistant anionic stacks, repeating along the short *b* axis, in which the co-ordination planes are tilted by 26.2° with respect to this axis. Within the stack the closest interionic atom–atom distances are simply the S ··· S

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* Ammonium bis(1,2-dicyanoethylene-1,2-dithiolato)nickelate hydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

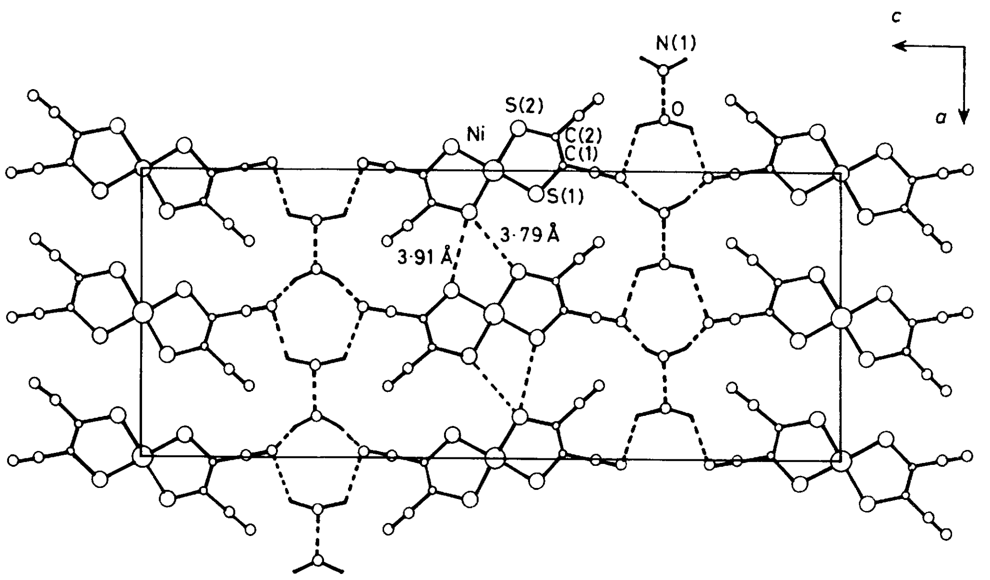

Figure 1. A view down the *b* axis of the crystal structure of $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$

Table 2. Important interatomic distances (Å) and interbond angles (°) for $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$

S(1)–Ni	2.151(3)	S(2)–Ni	2.152(3)
C(1)–S(1)	1.709(7)	C(2)–S(2)	1.717(7)
C(2)–C(1)	1.363(8)	C(10)–C(1)	1.445(7)
C(20)–C(2)	1.438(8)	N(10)–C(10)	1.131(7)
N(20)–C(20)	1.138(8)	H(10)–O	1.064(12)
H(2)–N(1)	1.050(2)	H(3)–N(1)	1.051(6)
H(4)–N(1)	1.068(14)		
S(2)–Ni–S(1)	93.1(5)	C(1)–S(1)–Ni	102.5(3)
C(2)–S(2)–Ni	102.5(3)	C(2)–C(1)–S(1)	121.2(5)
C(10)–C(1)–S(1)	119.1(5)	C(10)–C(1)–C(2)	119.7(6)
C(1)–C(2)–S(2)	120.6(5)	C(20)–C(2)–S(2)	118.6(5)
C(20)–C(2)–C(1)	120.8(6)	N(10)–C(10)–C(1)	177.8(7)
N(20)–C(20)–C(2)	177.0(6)	H(3)–N(1)–H(2)	100.5(72)
H(4)–N–H(2)	110.1(68)	H(4)–N(1)–H(3)	121.2(59)
H(10)–O–H(10)	103.8(76)	H(4)–N(1)–H(4)	93.7(74)
Selected non-bonded distances (Å)			
Intramolecular		Intermolecular	
S(2)–S(1)	3.124	S(2)–S(2c)	3.791
S(2)–S(1a)	2.958	S(2)–S(1b)	3.909

Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): (a) $-x$, $1.0 - y$, $1.0 - z$; (b) $-0.5 + x$, $0.5 - y$, z; (c) $-0.5 - x$, $-0.5 + y$, $1.0 - z$.

and Ni ··· Ni cell repeat distances. These are somewhat longer than those (3.639 Å) found for $Li_{0.82}(H_3O)_{0.33}[Pt\{S_2C_2(CN)_2\}_2]\cdot 1.67H_2O$ although the anion tilt is greater in the present complex and produces an interplanar perpendicular separation of 3.52 Å, now somewhat smaller than the spacing of 3.59 Å in the lithium salt. This is consistent with the magnetic properties of the compound which show localised electrons in the nickel complex as opposed to delocalised electrons in the platinum compound.

The stacks are arranged into sheets parallel to the *ab* face of the cell, separated by sheets of hydrogen-bonded cations and water molecules, which are further hydrogen-bonded to nitrogen atoms of one CN group of each thiolate ligand (see Figure 2). It is quite clear that this hydrogen bonding will have had some effect on the determination of the anion orientations and tilt. However, within the anionic sheets, neighbouring stacks are arranged such that the metal centres are stepped up by *b*/2 with inter-stack S ··· S contacts of 3.79 and 3.91 Å (see Figure 1). These contacts are significantly longer than the similarly arranged contacts in the lithium complex (3.68 and 3.74 Å)[2] and in $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$ (3.66 Å)[3] and are considerably greater than the van der Waals distance suggesting very little two-dimensional character in this compound.

The arrangement of anions of this type in adjacent stacks as observed in this compound has been discussed in detail by Hoffmann and co-workers[11] and attributed to the need to reduce S ··· S repulsions.

Structure at 98 K.—An attempt has been made to determine the structure at 98 K. A different crystal was used for this study and showed slightly different room-temperature cell dimensions to those given above. This is almost certainly a real effect and is most probably related to crystal quality (see above). Indeed the crystal quality was such that a complete determination of the crystal structure was not possible. However, oscillation photographs at 98 K showed that the *c*-axis spacing was doubled compared with that in the room-temperature structure. This indicates that dimerisation of the anions in the stack occurs at low temperatures. The average structure was determined using the main peaks and omitting the weak spots on odd layers because of the poor crystal quality. The average crystal structure at 98 K is essentially the same as that at room temperature. This indicates that when the anions in the stacks form dimers they do so in an eclipsed configuration similar to that previously observed in $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$ and not in the metal-over-sulphur arrangement found in $NEt_4[Ni\{S_2C_2(CN)_2\}_2]$.

General Discussion.—The arrangement of stacks of planar metal dithiolene anions to form two-dimensional sheets *via* interstack S ··· S contacts and separated by sheets of water molecules and cations found in $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ has been observed previously in other compounds.[2,3] In the case of $Li_{0.82}(H_3O)_{0.33}[Pt\{S_2C_2(CN)_2\}_2]\cdot 1.67H_2O$ the anions carry a non-integral negative charge and the resulting

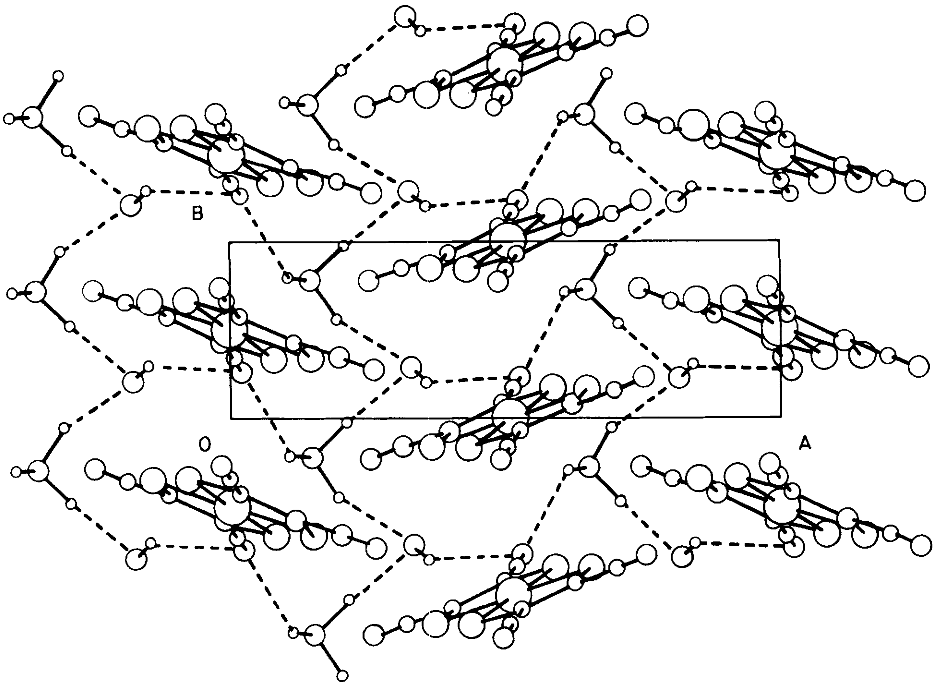

Figure 2. A view down the *c* axis showing the arrangement of components in the anion and cation/water sheets with hydrogen-bonding interactions marked by dashed lines

equidistant stack structure displays metallic properties.[1,2] In $Rb[Pt\{S_2C_2(CN)_2\}_2]\cdot H_2O$ the anions carry a single integral negative charge and the Peierls distortion results in a simple stack dimerisation.[3] The equidistant stack structure found for $NH_4[Ni\{S_2C_2(CN)_2\}_2]\cdot H_2O$ is therefore unexpected in view of the presence of the singly charged metal dithiolene monoanion. Metallic properties might be expected to be associated with the equidistant stack structure but the room-temperature conductivity is relatively low (5×10^{-2} Ω^{-1} cm^{-1}) and the compound exhibits the temperature dependence of a semi-conductor. It seems likely, therefore, that the equidistant stack of monoanions does not result in one-dimensional metallic properties because the on-site electron–electron repulsion, U, is much greater than $4t$ where t is the electron-transfer integral and therefore electrons are localised on individual molecules. The relative values of U and t will reflect the large intra- and inter-stack S $\cdots$ S distances observed in this compound. At room temperature, Isett *et al.*[5] showed that the compound they prepared behaved as an Heisenberg antiferromagnetic chain with $J = 300$ K. At low temperatures the behaviour was that of a singlet–triplet system with an activation energy $\Delta_m = 570$ K. The transition was observed to lie in the temperature range 130—200 K.

The magnetic properties at room temperature are consistent with the equidistant stack structure reported here. The transition to singlet–triplet behaviour below a transition temperature in the range 150—200 K suggests that dimerisation of the anions in the stack occurs below room temperature. The low-temperature structural studies reported here confirm that dimerisation in the stacking direction does occur and that therefore this is responsible for the observed singlet ground state. The transition temperature is too high for the transition to be driven by the energy stabilisation resulting from the singlet ground state (*i.e.* a spin Peierls transition). More likely the transition will be triggered by some other structural change in the lattice. At room temperature there is full occupancy of all the NH_4^+ sites with the hydrogen bonding producing a good rigid structure so that a simple ordering process is not responsible for the phase transition. Unfortunately a determination of the superstructure below the transition temperature was not possible although there is some evidence from the average structure of two potential water sites.

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