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Preparation, Structure, and Properties of $[Ni\{S_2C_2(CF_3)_2\}_2]^-$ and $[Ni\{Se_2C_2(CF_3)_2\}_2]^-$ Salts with Small Cations*

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The preparations, electrical conductivities, magnetic and spectroscopic properties of bis[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolato]nickelate, $[Ni\{S_2C_2(CF_3)_2\}_2]^-$, and bis[*cis*-1,2-bis(trifluoromethyl)-1,2-ethylenediselenato]nickelate, $[Ni\{Se_2C_2(CF_3)_2\}_2]^-$, salts with small counter ions are described.

Metal complexes of *cis*-1,2-bis(trifluoromethyl)-1,2-ethylenedithiolate, $S_2C_2(CF_3)_2{}^{2-}$, and *cis*-1,2-bis(trifluoromethyl)-1,2-ethylenediselenate, $Se_2C_2(CF_3)_2{}^{2-}$, are well known.[1–10] However, very little attention has been given to the synthesis and properties of simple salts containing mono- or di-anionic $[M\{S_2C_2(CF_3)_2\}_2]$ ions, and no work has been done on analogous $[M\{Se_2C_2(CF_3)_2\}_2]$ compounds (where M = Ni, Pd, or Pt). Previous work on $[M\{S_2C_2(CF_3)_2\}_2]$ has been confined to a tetraethylammonium salt and a detailed study of the salts of tetrathiafulvalene [2-(1′,3′-dithiol-2′-ylidene)-1,3-dithiole] and perylene cations.[4–8] The studies carried out on $[M\{Se_2C_2(CF_3)_2\}_2]$ compounds did not involve small cations, but rather salts where the counter ion is $AsPh_4{}^+$.[9]

During the past few years there has been renewed interest in $[M\{S_2C_2(CN)_2\}_2]$ (where M = Ni, Pd, or Pt) salts following the discovery that $(H_3O)_{0.33}Li_{0.8}[Pt\{S_2C_2(CN)_2\}_2]\cdot 1.67H_2O$ exhibits the properties of a one-dimensional metal.[11] More recent work has shown that the salts of $[Ni\{S_2C_2(CN)_2\}_2]^-$ with Group 1 metal cations and $NH_4{}^+$ exhibit unusual magnetic properties.[12] Work with metal complexes of the dithiolates $S_2C_2R_2{}^{2-}$ (R = Ph, Me, or H) failed to produce new one-dimensional metals.[13] It was proposed that these substituents R would result in a different electron distribution in the highest occupied molecular orbital compared with the case where R = CN. However, it has been suggested that the electron distribution in the $S_2C_2(CF_3)_2{}^{2-}$ complexes will be very similar to that of the $S_2C_2(CN)_2{}^{2-}$ complexes.[14] The greater spatial extension of the *4d* orbital on Se compared with the *3d* orbitals on S might be expected to lead to greater interanion interactions in the $Se_2C_2(CF_3)_2{}^{2-}$ complexes and hence higher electrical conductivities or increased magnetic interactions. In this paper we report on the preparation and properties of $[Ni\{S_2C_2(CF_3)_2\}_2]^-$ and $[Ni\{Se_2C_2(CF_3)_2\}_2]^-$ salts of small cations and compare them with analogous $S_2C_2(CN)_2{}^{2-}$ complexes. A preliminary account of the work on the $S_2C_2(CF_3)_2{}^{2-}$ compounds has been reported.[15]

Experimental

The ligands were prepared as previously described by the reaction of hexafluorobut-2-yne with boiling sulphur or selenium respectively.[9,16,17] The complexes $[Ni\{S_2C_2(CF_3)_2\}_2]$ and $[Ni\{Se_2C_2(CF_3)_2\}_2]$ were prepared by reaction of the respective ligand with $[Ni(CO)_4]$ in n-pentane at −5 °C.[1,2,9]

Preparation of Monoanion Salts.—The complex $[Ni\{S_2C_2(CF_3)_2\}_2]$ (*ca.* 1 g) was dissolved in acetone to produce a complex (acetone) $[Ni\{S_2C_2(CF_3)_3\}_2]^-$ species.[18] A 1 mol equivalent of the appropriate cation salt was added and the solvent removed under reduced pressure. The residue was dissolved in isobutyl alcohol–acetone (3:1) and the solvent allowed to evaporate slowly. The product crystallised out over a period of weeks, was filtered off, washed with isobutyl alcohol, and air dried.

The complex $[Ni\{Se_2C_2(CF_3)_2\}_2]$ (*ca.* 0.5 g) was reduced to the monoanion by dissolving it in methanol.[9] A 1 mol equivalent of the appropriate cation salt was added and the solvent removed under reduced pressure. The residue was recrystallised from toluene and air dried.

Preparation of Dianion salts.—The salts $[NEt_4]_2[Ni\{S_2C_2(CF_3)_2\}_2]$ and $[NEt_4]_2[Ni\{Se_2C_2(CF_3)_2\}_2]$ (air sensitive) were prepared by the literature method which involved reduction with hydrazine hydrate.[2]

Attempted Preparation of partially Oxidised Salts.—A variety of methods were used in the attempted preparation of partially oxidised $S_2C_2(CF_3)_2{}^{2-}$ salts, but none of them proved successful. These involved air-oxidation of $Li_2[Ni\{S_2C_2(CF_3)_2\}_2]$, electrocrystallisation of a solution of $Li_2[Ni\{S_2C_2(CF_3)_2\}_2]$, and co-crystallisation of a solution of this salt with $Li[Ni\{S_2C_2(CF_3)_2\}_2]$. The last method gave black crystals of indeterminate composition which exhibited electrical conduction properties similar to the monoanion salt.

Results and Discussion

Using the experimental procedures described above it has been found possible to prepare a series of $[Ni\{S_2C_2(CF_3)_2\}_2]^-$ and $[Ni\{Se_2C_2(CF_3)_2\}_2]^-$ salts of K^+, Na^+, Rb^+, $NH_4{}^+$, Cs^+, Li^+, $NEt_4{}^+$, and $NBu_4{}^+$. Both series of salts are anhydrous in contrast to the corresponding $[Ni\{S_2C_2(CN)_2\}_2]^-$ salts which are obtained as hydrates. This is presumably due to the replacement of hydrophilic CN groups on the ligand by the hydrophobic CF_3 group since crystal structure determinations have indicated hydrogen bonding between the water molecules and the CN substituents on the ligands in the $[Ni\{S_2C_2(CN)_2\}_2]^-$ complexes.[19]

Table 1 lists the analytical data for the compounds and the physical properties of the compounds are given in Table 2. The room-temperature magnetic moment of $[NEt_4][Ni\{S_2C_2(CF_3)_2\}_2]$ determined during the course of this work is similar to that previously reported and indicates one unpaired electron per anion.[1] Variable-temperature susceptibility measurements of this compound down to low temperature show simple Curie–Weiss behaviour.[20] This is in contrast to the behaviour of $[NEt_4][Ni\{S_2C_2(CN)_2\}_2]$ which exhibits singlet–triplet equilibria as a result of the association of the anions in dimer pairs.[21] Thus it appears that the $[Ni\{S_2C_2(CF_3)_2\}_2]^-$ anions are present as isolated species in the crystal. The room-temperature magnetic moments of all the $[Ni\{S_2C_2(CF_3)_2\}_2]^-$ salts of small

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* *Non-S.I. unit employed:* B.M. ≈ 9.27×10^{-24} A m^2.

Table 1. Analysis (%) of compounds

	Theoretical			Found		
Compound	C	H	N	C	H	N
$[\mathrm{NEt_4}][\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	37.3	5.2	3.6	36.7	5.3	3.5
$[\mathrm{NBu_4}][\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	38.5	4.5	1.8	38.2	4.2	1.9
$\mathrm{Li[Ni\{S_2C_2(CF_3)_2\}_2]}$	18.5			18.2		
$\mathrm{Na[Ni\{S_2C_2(CF_3)_2\}_2]}$	18.0			17.5		
$\mathrm{K[Ni\{S_2C_2(CF_3)_2\}_2]}$	17.4			16.9		
$\mathrm{Rb[Ni\{S_2C_2(CF_3)_2\}_2]}$	16.1			15.9		
$[\mathrm{NH_4}][\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	18.1	0.8	2.6	18.5	1.1	2.9
$\mathrm{Cs[Ni\{S_2C_2(CF_3)_2\}_2]}$	14.9			14.2		
$[\mathrm{NEt_4}]_2[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	29.9	3.1	2.2	31.0	3.4	2.9
$[\mathrm{NEt_4}][\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	23.2	2.4	1.7	23.6	3.1	1.9
$\mathrm{Li[Ni\{Se_2C_2(CF_3)_2\}_2]}$	13.6			13.3		
$\mathrm{Na[Ni\{Se_2C_2(CF_3)_2\}_2]}$	13.3			13.9		
$\mathrm{K[Ni\{Se_2C_2(CF_3)_2\}_2]}$	13.0			13.5		
$\mathrm{Rb[Ni\{Se_2C_2(CF_3)_2\}_2]}$	12.2			12.6		
$[\mathrm{NH_4}][\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	13.4	0.6	1.9	13.9	0.9	1.8
$\mathrm{Cs[Ni\{Se_2C_2(CF_3)_2\}_2]}$	11.5			11.9		
$[\mathrm{NEt_4}]_2[\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	27.5	4.1	2.9	27.8	4.5	3.6
$[\mathrm{NBu_4}][\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	38.2	4.8	1.8	38.4	5.6	1.4

cations are very similar to each other and indicate that in each case the anion is present as an isolated species.

The reflectance spectra of the $[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]^-$ complexes are very similar to each other and all exhibit an intense absorption at *ca.* 12 500 cm^{-1}, similar in position to the band observed for this ion in acetone solution.[1] The similarity in the position of the band in solution and the solid state indicates that the energy levels are not perturbed by solid-state interactions and again indicates that the $[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]^-$ anion exists as isolated species in the solid state in all the compounds studied.

The magnetic moments of all the $[\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]^-$ salts apart from that of $\mathrm{Li^+}$ are consistent with the presence of one unpaired electron per anion. The salt $\mathrm{Li[Ni\{Se_2C_2(CF_3)_2\}_2]}$ has a room-temperature magnetic moment of 1.12 B.M. This is lower than the expected value and could indicate antiferromagnetic coupling of the unpaired electrons on adjacent molecules due to the presence of anion dimers. The diffuse reflectance spectra of $\mathrm{A[Ni\{Se_2C_2(CF_3)_2\}_2]}$ (A = Li, Na, K, or $\mathrm{NH_4}$) all show broad ill defined absorptions. However, the reflectance spectra of the corresponding salts of $\mathrm{Cs^+}$, $\mathrm{Rb^+}$, $\mathrm{NEt_4{}^+}$, and $\mathrm{NBu_4{}^+}$ show an intense absorption at *ca.* 12 500 cm^{-1} with a shoulder at 15 500 cm^{-1}.

The electrical conductivities were determined using the four-probe d.c. technique on compressed pellets of the compounds except for $\mathrm{A[Ni\{S_2C_2(CF_3)_2\}_2]}$ (A = $\mathrm{NEt_4}$ or $\mathrm{NBu_4}$) which were measured along the needle axis of a single crystal and $[\mathrm{NEt_4}]_2[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$ which was measured across one of the faces of the cube-shaped crystal. The conductivities are low and in the range 10^{-5}—10^{-8} S cm^{-1}.

These values are similar to those of the $[\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^-$ salts of the same cations, apart from $\mathrm{NH_4{}^+}$, although their magnetic properties are quite different.[11]

The results obtained above for the $[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]^-$ and $[\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]^-$ salts contrast sharply with those of the $[\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^-$ salts of the same cations. For all the $\mathrm{S_2C_2(CF_3)_2{}^{2-}}$ and $\mathrm{Se_2C_2(CF_3)_2{}^{2-}}$ complexes, apart possibly from $\mathrm{Li[Ni\{Se_2C_2(CF_3)_2\}_2]}$, the anions are present in the lattice as isolated ions. In the salts of $[\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^-$ with large cations (*e.g.* $\mathrm{NEt_4{}^+}$) the anions are associated as ion pairs with an intra-dimer separation of *ca.* 3.5 Å. The salts of small cations (*e.g.* $\mathrm{NH_4{}^+}$ or $\mathrm{Na^+}$) contain the anions arranged in an equidistant stack structure with inter-ion separation of <4 Å at room temperature and the resulting magnetic interactions gave rise to the behaviour of a Heissenberg antiferromagnetic chain. Clearly in the salts of $[\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]^-$ and $[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]^-$ the inter-anion separation must be >4 Å. Since the electron distribution in the latter complex is expected to be the same as in the $\mathrm{S_2C_2(CN)_2{}^{2-}}$ complex the large inter-ion separation is probably due to steric factors associated with the replacement of the linear C≡N group with the much larger $\mathrm{CF_3}$ group. In view of the absence of interactions in the monoanion salts it is perhaps not surprising that all attempts to prepare one-dimensional metals based on $[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]^-$ were unsuccessful.

Table 2. Physical properties of $[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]^{n-}$ and $[\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]^{n-}$ salts

Compound	Electrical conductivity* (S cm^{-1})	Magnetic moment* (B.M.)
$[\mathrm{NEt_4}][\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	4.2×10^{-7} (s.c.)	1.80
$[\mathrm{NBu_4}][\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	2.2×10^{-6} (s.c.)	1.79
$\mathrm{Li[Ni\{S_2C_2(CF_3)_2\}_2]}$	4.2×10^{-5} (c.p.)	1.57
$\mathrm{Na[Ni\{S_2C_2(CF_3)_2\}_2]}$	2.3×10^{-5} (c.p.)	1.77
$\mathrm{K[Ni\{S_2C_2(CF_3)_2\}_2]}$	5.2×10^{-6} (c.p.)	1.55
$\mathrm{Rb[Ni\{S_2C_2(CF_3)_2\}_2]}$	3.1×10^{-6} (c.p.)	1.54
$[\mathrm{NH_4}][\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	6.5×10^{-5} (c.p.)	1.80
$\mathrm{Cs[Ni\{S_2C_2(CF_3)_2\}_2]}$	1.2×10^{-6} (c.p.)	1.52
$[\mathrm{NEt_4}]_2[\mathrm{Ni\{S_2C_2(CF_3)_2\}_2}]$	6.2×10^{-8} (s.c.)	Diamagnetic
$[\mathrm{NEt_4}][\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	2.6×10^{-8} (c.p.)	1.98
$[\mathrm{NBu_4}][\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	2.1×10^{-8} (c.p.)	1.96
$\mathrm{Li[Ni\{Se_2C_2(CF_3)_2\}_2]}$	5.2×10^{-5} (c.p.)	1.12
$\mathrm{Na[Ni\{Se_2C_2(CF_3)_2\}_2]}$	7.0×10^{-6} (c.p.)	1.96
$\mathrm{K[Ni\{Se_2C_2(CF_3)_2\}_2]}$	8.8×10^{-6} (c.p.)	1.92
$\mathrm{Rb[Ni\{Se_2C_2(CF_3)_2\}_2]}$	4.1×10^{-6} (c.p.)	1.92
$[\mathrm{NH_4}][\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	2.4×10^{-6} (c.p.)	1.91
$\mathrm{Cs[Ni\{Se_2C_2(CF_3)_2\}_2]}$	3.5×10^{-6} (c.p.)	2.23
$[\mathrm{NEt_4}]_2[\mathrm{Ni\{Se_2C_2(CF_3)_2\}_2}]$	1.2×10^{-8} (c.p.)	Diamagnetic

* Recorded at room temperature; c.p. = compressed pellet, s.c. = single crystal (see text).

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