# $[Ni(edt-CN)_2]^{-\cdot}$, a novel paramagnetic nickel dithiolene complex analog of $Ni(mnt)_2^{-\cdot}$ with two cyano groups only

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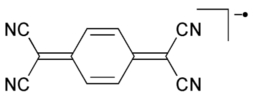
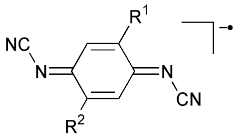
**The preparation, X-ray crystal structures and electrochemical properties of bis(2-cyano-1,2-ethanedithiolate)-nickelate $[Ni(edt-CN)_2]^{2-/-\cdot}$ are described for both oxidation states together with the singlet–triplet behaviour of the $PPh_4^+$ salt of the paramagnetic $[Ni(edt–CN)_2]^{-\cdot}$ complex.**

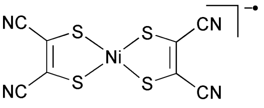
The construction of conducting or magnetic solids from the assembling of transition metal centers and organonitrile anion radical molecules[1] such as $TCNE^{-\cdot}$, $DCNQI^{-\cdot}$ or $TCNQ^{-\cdot}$ has revealed extraordinary materials such as the metallic $Cu(DCNQI)_2$,[2] the electrically bistable[3] Cu(TCNQ) or a bulk ferromagnet from V with TCNE (TCNE = tetracyanoethylene).[4] By comparison and most surprisingly, the parallel coordination chemistry of the corresponding nickel dithiolene complexes with the maleonitriledithiolate ligand ($mnt^{2-}$) is virtually untouched and only a few salts of the diamagnetic $Ni(mnt)_2^{2-}$ have been reported with $Ag(PPh_3)_2^+$ and CuI.[5,6] The crystalline salts derived from DCNQI anions incorporating only two nitrile groups as well as the rich chemistry of the $mnt^{2-}$ complexes[7] prompted us to investigate the numerous possibilities that would be offered by the unknown corresponding nickel dithiolene complex bearing only two cyano groups, *viz.* bis(2-cyano-1,2-ethanedithiolate)nickelate $[Ni(edt-CN)_2]^{n-}$ ($n$ = 1 or 2). We describe here the synthesis of this novel complex system together with its electrochemical properties and report and analyse the X-ray crystal structures of the $PPh_4^+$ salts of both the diamagnetic $[Ni(edt-CN)_2]^{2-}$ dianion and the paramagnetic radical anion $[Ni(edt-CN)_2]^{-\cdot}$. This complex offers extensive possibilities for the elaboration of promising materials with conducting or magnetic properties by varying the nature of the counter cation, closed-shell inorganic ($Na^+$, $Cu^+$, $Ag^+$ or $NH_4^+$) or organic ($R_4N^+$, $PyH^+$, ...) cations as well as open shell organic ($TTF^{+\cdot}$, $BEDT\text{-}TTF^{+\cdot}$) or organometallic ($Cp^*_2Fe^{+\cdot}$) cations.



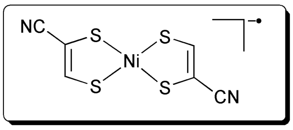
**TCHNQ$^{-\bullet}$**



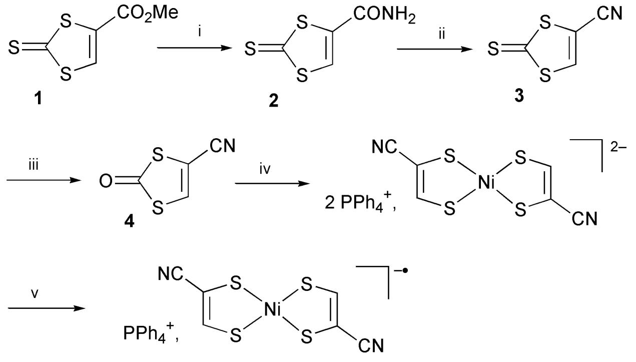
**DCHNQI$^{-\bullet}$**



**Ni(mnt)$_2$$^{-\bullet}$**



**Ni(edt-CN)$_2$$^{-\bullet}$**



**Scheme 1** *Reagents and conditions*: i, $NH_3$/MeOH; ii, 1 equiv. $POCl_3$, tetramethylene sulfone, 100 °C, 7 h; iii, $Hg(OAc)_2$, $CHCl_3$–AcOH, 2 h; iv, 2 equiv. MeONa, MeOH, 0.5 $NiCl_2\cdot6H_2O$, $PPh_4Cl/H_2O$; v, 0.5 $I_2$.

The dithiocarbonate **4**† precursor of the dithiolene ligand was prepared by a novel route (Scheme 1) which avoids the use of cyanoacetylene[8] in the reported preparation of **3** or that of activated Zn complexes in the reported preparation of **4**.[9] The easily available ester **1**[10] was successively converted into the corresponding amide **2** with $NH_3$ in MeOH in 72% yield, into the nitrile **3** by $POCl_3$ dehydration[11] in 75% yield before oxymercuration to the dithiocarbonate **4** in 84% yield. Treatment of **4** with 2 equiv. of MeONa followed by addition of 0.5 equiv. $NiCl_2\cdot6H_2O$ and $PPh_4Cl$ afforded the air-stable dianionic diamagnetic $[PPh_4^+]_2[Ni(edt-CN)_2^{2-}]$ salt. The corresponding one-electron oxidation product, $[PPh_4^+][Ni(edt-CN)_2^{-\cdot}]$, was obtained by iodine oxidation and recrystallisation from methanol. Cyclic voltammetry of the dianionic $Ni(edt-CN)_2^{2-}$ salt (Fig. 1) shows that it oxidises reversibly to the monoanionic $Ni(edt-CN)_2^{-\cdot}$ at −0.31 V *vs.* SCE while an irreversible process is observed at +0.65 V, a behaviour also observed for $Ni(mnt)_2^{n-}$ (0.226 V for $Ni(mnt)_2^{2-/-}$ with an ill-defined oxidation wave around 1 V)[12] but with a cathodic shift attributable to the presence of only two cyano groups. Single crystal X-ray structures‡ of both salts show that the nickel complexes adopt the same square-planar structure in the two different oxidation states (Fig. 2) with a *trans* orientation of the two cyano groups. It is likely that both *cis* and *trans* orientations are in equilibrium in solution while the most symmetrical *trans* isomer exhibits a lower solubility. The observed shortening of the Ni–S and C–S bonds upon oxidation of the dianion to the monoanion is in accordance with the antibonding character of

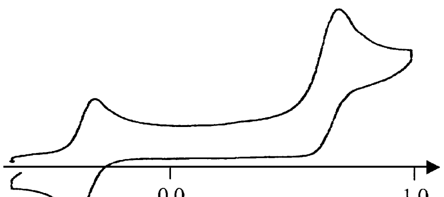


**Fig. 1** Cyclic voltammetry of $[PPh_4]_2[Ni(edt-CN)_2]$, in MeCN with 0.5 M $NBu^n_4PF_6$ as electrolyte at a scan rate of 100 mV $s^{-1}$.

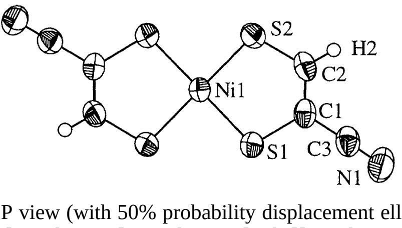


**Fig. 2** ORTEP view (with 50% probability displacement ellipsoids) of the radical anion $[Ni(edt-CN)_2]^{-\cdot}$ in the 1 : 1 $[PPh_4][Ni(edt-CN)_2]$ salt.

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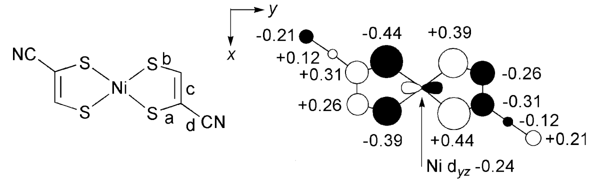
**Table 1** Important bond distances (Å) in $[Ni(edt\text{-}CN)_2]^{2-/-\cdot}$ together with a representation of the π-type HOMO of $[Ni(edt\text{-}CN)_2]^{2-}$



| | $[Ni(edt\text{-}CN)_2]^{2-}$ | $[Ni(edt\text{-}CN)_2]^{-\cdot}$ |
|---|---|---|
| Ni–S | 2.188(2) | 2.148(3) |
| S–C (bond a) | 1.756(5) | 1.736(3) |
| S–C (bond b) | 1.720(5) | 1.706(4) |
| C=C (bond c) | 1.342(7) | 1.341(4) |
| C–C (bond d) | 1.426(8) | 1.427(4) |
| C≡N | 1.148(7) | 1.141(3) |

those bonds in the dianion HOMO shown in Table 1. Similarly the antibonding character of the C≡N bonds is reflected by an increase in ν(C≡N), from 2180 $cm^{-1}$ in the dianion to 2205 $cm^{-1}$ in the monoanion. In the 2:1 $[PPh_4^+]_2[Ni(edt\text{-}CN)_2^{2-}]$ salt, two crystallographically independent dianions, each of them on an inversion centre, are fully isolated from each other by the bulky $PPh_4^+$ cations. On the other hand, in the 1:1 $[PPh_4^+][Ni(edt\text{-}CN)_2^{-\cdot}]$ salt, the open-shell anions, in general positions in the unit cell, associate into inversion-centered diads with a unusual overlap (Fig. 3) and a short plane-to-plane distance of 3.519(3) Å. The temperature dependence of the SQUID magnetic susceptibility for this salt (Fig. 4) exhibits a maximum at 23 K and is satisfactorily fitted with the Bleaney–Bowers[13] expression of the susceptibility[14] of singlet–triplet behaviour with $|J/k|$ = 37.5(2) K, in accordance with the diad structure. Preliminary metathesis experiments show that a highly insoluble precipitate is obtained upon addition of $AgBF_4$ to $[PPh_4^+][Ni(edt\text{-}CN)_2^{-\cdot}]$ solutions while the $Cu^+$ salt obtained from $Cu(MeCN)_4BF_4$ is much more soluble. Charge-transfer salts are also being investigated with organic ($TTF^{+\cdot}$) and organometallic ($Cp^*_2Fe^{+\cdot}$) radical cations as well as with functionalized TTF molecules bearing hydrogen bonding groups or halogen atoms able to interact in the solid state with the cyano group.

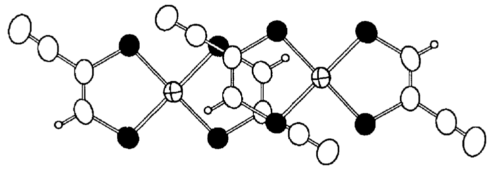


**Fig. 3** The peculiar overlap between two $[Ni(edt\text{-}CN)_2]^{-\cdot}$ radical anions in the 1:1 $[PPh_4][Ni(edt\text{-}CN)_2]$ salt.

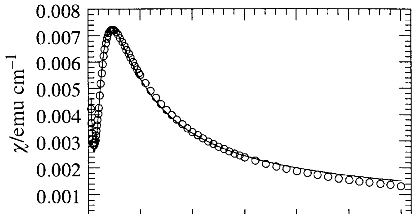


**Fig. 4** Temperature dependence of the magnetic susceptibility of the 1:1 $[PPh_4][Ni(edt\text{-}CN)_2]$ salt. The solid line is a fit to the Bleaney–Bowers equation (see text) together with a low-temperature Curie tail encompassing 2.7% magnetic defects.

## Notes and references

† *Selected data* for **2**: yellow crystals; mp 225–226 °C (MeOH), $\delta_H$(400 MHz, $d_6$-DMSO), 3.36 (s, 2H, $NH_2$), 8.18 (s, 1H, CH); $\delta_C$(100 MHz, $d_6$-DMSO), 134.2 (CH), 143.7 ($CCONH_2$), 160.0 (C=O), 213.9 (C=S). $\nu_{max}$(KBr)/$cm^{-1}$; 1651 (C=O), 1084 (C=S). MS (EI) *m/z* (%) 177 (100, $M^{\cdot+}$) (Anal. Calc. for $C_4H_3NOS_3$ (177.35): C, 27.19; H, 1.71; N, 7.90; S, 54.27. Found: C, 27.19; H, 1.67; N, 7.71; S, 53.32%). For **3**: yellow crystals; mp 96 °C (lit.:[8] 100–101 °C, $\delta_H$(400 MHz, $CDCl_3$), 7.73 (s, 1H, CH); $\delta_C$(100 MHz, $CDCl_3$), 109.7 (*C*CN), 112.2 (C≡N), 142.3 (CH), 207.7 (C=S). $\nu_{max}$(KBr)/$cm^{-1}$; 1058 (C=S), 2218 (C≡N). MS (EI) *m/z* (%) 159 (100, $M^{\cdot+}$) (Anal. Calc. for $C_4HNS_3$ (159.257): C, 30.17; H, 0.63; N, 8.80; S, 60.40. Found: C, 30.14; H, 0.70; N, 8.28; S, 60.1%). For **4**: white crystals; mp 60–63 °C, $\delta_H$(400 MHz, $CDCl_3$), 7.61 (s, 1H, CH); $\delta_C$(100 MHz, $CDCl_3$), 103.7 (*C*CN), 111.3 (C≡N), 134.0 (CH), 188.0 (C=O). $\nu_{max}$(KBr)/$cm^{-1}$; 1636 (C=O), 2229 (C≡N). (lit.:[9] 1638, 2235), MS (EI) *m/z* (%) 143 (100, $M^{\cdot+}$) (Anal. Calc. for $C_4HNOS_2$ (143.190): C, 33.57; H, 0.70; N, 9.79; S, 44.76. Found: C, 33.78; H, 0.83; N, 9.43; S, 43.68%). For $[PPh_4]_2[Ni(edt\text{-}CN)_2]$: $\nu_{max}$(KBr)/$cm^{-1}$; 2180 (C≡N). (Anal. Calc. for $C_{54}H_{42}N_2NiPS_4$ (967.85): C, 67.01; H, 4.37; N, 2.89; S, 13.25. Found: C, 66.61; H, 4.21; N, 2.84; S, 13.41%). For $[PPh_4][Ni(edt\text{-}CN)_2]$: $\nu_{max}$(KBr)/$cm^{-1}$; 2204 (C≡N). (Anal. Calc. for $C_{30}H_{22}N_2NiPS_4$ (628.45): C, 57.34; H, 3.53; N, 4.46. Found: C, 57.09; H, 3.47; N, 4.32%).

‡ *X-Ray data* for $[PPh_4]_2[Ni(edt\text{-}CN)_2]$ and $[PPh_4][Ni(edt\text{-}CN)_2]$ were collected on a Stoe Imaging Plate diffractometer (IPDS) with Mo-Kα radiation, $\lambda$ = 0.71073 Å at $T$ = 293(2) K. The structures were solved by direct methods and refined against $F^2$ using the SHELXTL5.04 set of programs. Hydrogen atoms were introduced at calculated positions and not refined (riding model).

*Crystal data* for $[PPh_4]_2[Ni(edt\text{-}CN)_2]$: $C_{54}H_{42}N_2NiP_2S_4$, $M$ = 967.79, monoclinic, space group $P2_1/n$, $a$ = 20.523(4), $b$ = 11.220(2), $c$ = 21.304(4) Å, $\beta$ = 107.33(3)°, $V$ = 4683(1) Å$^3$, $Z$ = 4, $D_c$ = 1.373 g $cm^{-3}$, $\mu$ = 0.701 $mm^{-1}$, data collected = 35954, unique data = 9096 ($R_{int}$ = 0.061) of which 5396 with $I > 2\sigma(I)$, $R(F)$ = 0.058, $wR(F^2)$ = 0.163 for 571 parameters.

For $[PPh_4][Ni(edt\text{-}CN)_2]$: $C_{30}H_{22}N_2NiPS_4$, M = 628.42, triclinic, space group $P\bar{1}$, $a$ = 11.394(1), $b$ = 11.510(1), $c$ = 12.826(1) Å, $\alpha$ = 64.264(10), $\beta$ = 72.777(12), $\gamma$ = 83.074(12)°, $V$ = 1447.2(3) Å$^3$, $Z$ = 2, $D_c$ = 1.442 g $cm^{-3}$, $\mu$ = 1.037 $mm^{-1}$, data collected = 14189, unique data = 5232 ($R_{int}$ = 0.042) of which 3582 with $I > 2\sigma(I)$, $R(F)$ = 0.0343, $wR(F^2)$ = 0.0713 for 343 parameters.

CCDC 182/1779. See http://www.rsc.org/suppdata/cc/b0/b006440h/ for crystallographic files in .cif format.

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