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A Simple Approach to Coordination Compounds of the Pentacyanocyclopentadienide Anion

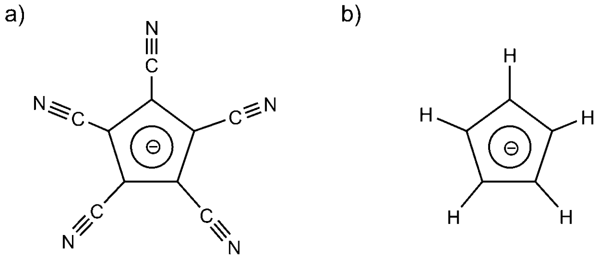
Robert J. Less, Mary McPartlin, Jeremy M. Rawson, Paul T. Wood,* and Dominic S. Wright*[a]

Abstract: Deprotonation of [Et_3NH][$C_5(CN)_5$] with metal bases provides a very simple approach to coordination compounds containing the pentacyanocyclopentadienide anion [$C_5(CN)_5$]$^-$ (**1**). The three-dimensional polymer [$Na(thf)_{1.5}$(**1**)]$_\infty$ and the molecular dimer [{$(tmeda)_2Na$(**1**)}$_2$] are obtained by reaction of this precursor with NaH in the presence of thf or tmeda ($Me_2NCH_2CH_2NMe_2$). Their single-crystal X-ray structures both reveal σ-bonded C≡N−Na arrangements and π stacking between [$C_5(CN)_5$]$^-$ ions. DFT calculations on the [$C_5(CN)_5$]$^-$ ion have been used to investigate the structures and bonding in [$Na(thf)_{1.5}$(**1**)]$_\infty$ and [{$(tmeda)_2Na$(**1**)}$_2$]. The absence of π bonding of the metal ions in both complexes is due to dispersion of the negative charge from the C_5 ring unit to the C≡N groups in the [$C_5(CN)_5$]$^-$ ion, making the coordination chemistry of this anion distinctly different from that of cyclopentadienide $C_5H_5^-$.

Keywords: coordination chemistry · density functional calculations · pentacyanocyclopentadienide · sodium · X-ray diffraction

Introduction

Although the pentacyanocyclopentadienide anion, [$C_5(CN)_5$]$^-$ (**1**) (Scheme 1 a), was first prepared as long ago as 1966,[1] surprisingly little is known about its structural and coordination chemistry.[2] What is clear so far is that substitution of the H atoms of the cyclopentadienide anion (Scheme 1 b) with electron-withdrawing CN groups results in a high degree of charge-transfer from the C_5-ring unit to the CN periphery. This can be seen to have three major effects on the behaviour of the pentacyanocyclopentadienide anion: 1) the C_5 unit has stronger π-acceptor character than Cp$^-$, forming π-stacked complexes with electron-rich organic π systems,[2a–c] 2) the [$C_5(CN)_5$]$^-$ ion is only a moderately weakly coordinating anion,[2c] with the conjugate acid [$C_5(CN)_5$]H being a strong acid, and 3) metal coordination is likely to occur through σ bonding of the peripheral CN groups[2d] rather than in the conventional manner for other cyclopentadienide derivatives through π bonding of the C_5-ring unit.[3]



Scheme 1. a) The pentacyanocyclopentadienide anion (**1**) and b) the cyclopentadienide anion.

There has been considerable world-wide interest in the preparation of multidimensional metal–organic coordination polymers that incorporate interesting, true lower-symmetry magnetic lattices. Organic ligands such as squaric (C_4O_4H)[4] and mellitic acid (1,2,3,4,5,6-[$C_6(CO_2H)_6$])[5] acid have been employed extensively as four-fold and six-fold symmetric ligands in this setting. Our current interest in **1** is that it represents a unique example of a five-fold symmetric nodal ligand for the preparation of magnetic lattices. As noted by Williams and co-workers, the planar D_{5h} symmetry of this anion may also lead to the self-assembly of spheroidal structures in which linear metal geometries are present, related to the topography of buckminsterfulerene, C_{60}.[2d] However,

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[a] Dr. R. J. Less, Prof. M. McPartlin, Dr. J. M. Rawson,
Prof. P. T. Wood, Prof. D. S. Wright
Chemistry Department, Cambridge University
Lensfield Road, Cambridge CB4 1DF (UK)
E-mail: dsw1000@cam.ac.uk

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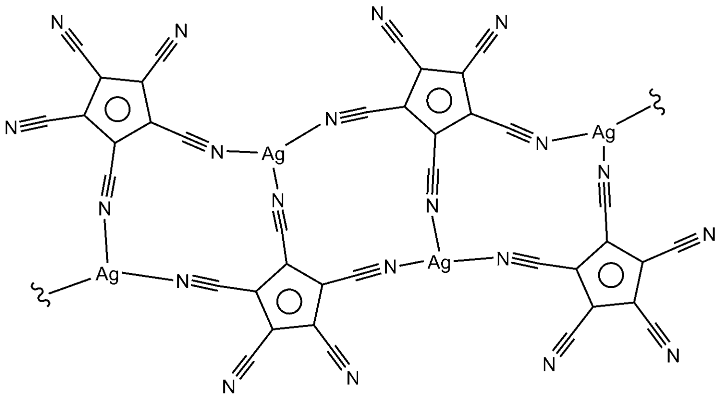
it can be noted in this regard that in practice a powder diffraction study of the Ag^I salt [Ag(**1**)] showed it to have a polymeric arrangement in which three-coordinate Ag^+ ions are linked into a sheet structure by three of the five CN groups of each of the anions (Scheme 2).[2d] As a first step in our studies we present here a simple approach by which in theory *any* metal salt of **1** can be readily prepared at low temperature, provided a basic source of the metal is available (this could be, for example, an organometallic reagent, a metal amide, or indeed the metal itself). Polymeric $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and dimeric $[\{(tmeda)_2Na(\mathbf{1})\}_2]$ are the first metal salts of **1** to be characterised by single-crystal X-ray analysis and (in themselves) represent key starting materials for transfer of **1** to other metals.



Scheme 2. Structure of [Ag(**1**)], obtained from a powder diffraction study.

Results and Discussion

The only synthetic strategy currently employed for the formation of complexes of **1** is the metathesis reaction of tetraalkyl ammonium salts $[R_4N][\mathbf{1}]$ with organic precursors or metal salts [Eq. (1)].[2] During preliminary studies of the formation of a range of metal complexes, however, we have found that this method frequently does not work cleanly and more often than not only the starting salts $[R_4N][\mathbf{1}]$ were recovered from reactions after crystallisation. The major drawback of this approach is its reliance on the lattice energy of the products to provide the thermodynamic driving force. Thus, the choice of $[R_4N]^+$ and X^- appears to be critical to the success of the reaction.

$$[R_4N][\mathbf{1}] + MX \longrightarrow [R_4N]X + M[\mathbf{1}] \qquad (1)$$

It occurred to us that deprotonation of the conjugate acid [**1**H] would provide the broadest synthetic approach, paralleling the methodology used for CpH in organometallic chemistry. However, as noted by Reed and co-workers 'the acid is extremely sensitive to moisture making it difficult to obtain and store in high purity.'[2c] We therefore opted to use the trimethylammonium salt $[Et_3NH][\mathbf{1}]$ as a synthon for [**1**H]. Although $[Et_3NH][\mathbf{1}]$ has been used as a precursor in methathesis reactions previously, to our knowledge, it has not been employed as an acid synthon before.[6] As a demonstration of this methodology we applied this approach firstly to the synthesis of the sodium salts $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and $[\{(tmeda)_2Na(\mathbf{1})\}_2]$ [Eq. (2)], being interested in the fundamental structural differences between the sodium salts of **1** and Cp^-.

$$[Et_3NH][\mathbf{1}] + NaH \xrightarrow[\substack{L = \text{thf } (n = 1.5) \\ \text{tmeda } (n = 2)}]{nL} Na[\mathbf{1}].nL + H_2\uparrow + Me_3N\uparrow \qquad (2)$$

The anion **1** was obtained by the literature procedure from the reaction of $[SC(CN){=}C(CN)]_2$ with $[CH(CN)(CO_2Me)]^-$.[7] The salt $[Et_3NH][\mathbf{1}]$ was precipitated from the reaction and crystallised from water in 33 % yield. This material was thoroughly dried under vacuum prior to further reactions. The reaction of $[Et_3NH][\mathbf{1}]$ with NaH in thf or tmeda gives $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ (in 80 % crystalline yield) and $[\{(tmeda)_2Na(\mathbf{1})\}_2]$ (35 % crystalline yield), respectively. NMR spectroscopic and elemental analysis indicated that isolation of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ (10^{-1} atm, ca. 15 min) led to complete loss of the coordinated thf ligands, giving the desolvated salt [Na(**1**)]. For $[\{(tmeda)_2Na(\mathbf{1})\}_2]$, the loss of up to 0.5 of a molecule of tmeda per Na^+ ion occurs by drying of the crystalline complex under an argon stream during isolation. The ^{13}C NMR chemical shifts for the C≡N (ca. $\delta = 113$ ppm) and C_5-ring (ca. $\delta = 102$ ppm) carbon atoms of the $[C_5(CN)_5]^-$ ion are very similar for $[Et_3NH][\mathbf{1}]$ $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and $[\{(tmeda)_2Na(\mathbf{1})\}_2]$, indicating that similar charge distributions are present in the anions of all of the compounds.

The low-temperature X-ray structures of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and $[\{(tmeda)_2Na(\mathbf{1})\}_2]$ were obtained, and for completeness so was that of the precursor $[Et_3NH][\mathbf{1}]$. Details of the data collections and refinements are summarised in Table 1 (see Experimental Section). In Figure 1–3 C-bonded H atoms are omitted for clarity.

The solid-state structure of the precursor $[Et_3NH][\mathbf{1}]$ consists of ion pairs of the monomer units, which are associated by H-bonding between the H atom of the $[Et_3NH]^+$ ion and one of the N atoms of the $[C_5(CN)_5]^-$ ion (Figure 1). The the distinctly bent geometry of the N–H···N interaction suggests weak H-bonding, as expected for the relatively weakly coordinating character of the $[C_5(CN)_5]^-$ ion [N1···N6 3.015(2) Å; N6–H···N6 2.15(1), 154.9(1)°].[8] The $[C_5(CN)_5]^-$ ions then form π-stacked columns, which aligned along the crystallographic *c* axis. The off-set C_5-ring planes are almost parallel and are separated by approximately 3.40 Å. This is consistent with the presence of weak graphitic type interactions.[9] Notably, the shortest C···C contacts involved occur

Table 1. Crystal data and structure refinements for $[Me_3NH][\mathbf{1}]$, $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and $[\{(tmeda)_2Na(\mathbf{1})\}_2]$.[a]

	$[Me_3NH][\mathbf{1}]$	$[Na(thf)_{1.5}(\mathbf{1})]_\infty$	$[\{(tmeda)_2Na(\mathbf{1})\}_2]$
empirical formula	$C_{16}H_{16}N_6$	$C_{32}H_{24}N_{10}Na_2O_3$	$C_{44}H_{64}N_{18}Na_2$
fw	292.35	642.59	891.11
crystal system	monoclinic	orthorhombic	Orthorhombic
space group	*P*21/*c*	*Fdd*2	*Pca*2(1)
a [Å]	11.5089(3)	22.3092(5)	26.6890(1)
b [Å]	21.5377(9)	41.769(1)	9.4462(2)
c [Å]	6.7981(5)	7.1646(1)	20.9747(4)
β [°]	95.920(2)	–	–
Z	4	8	4
V [Å^3]	1676.09(15)	6676.2(2)	5287.92(15)
ρ_{calcd} [mg m^{-3}]	1.159	1.279	1.119
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.074	0.109	0.086
reflns collected (R_{int})	11 562 (0.051)	13 597 (0.037)	31 396 (0.035)
θ range [°]	3.56–24.99	3.56–26.37	1.53–27.49
indep. reflns (R_{int})	2885	1844	6167
R indices [$I > 2\sigma(I)$]	$R1 = 0.043$, $WR2 = 0.103$	$R1 = 0.043$, $WR2 = 0.098$	$R1 = 0.042$, $WR2 = 0.109$
R indices (all data)	$R1 = 0.065$, $WR2 = 0.112$	$R1 = 0.063$, $WR2 = 0.109$	$R1 = 0.058$, $WR2 = 0.123$
absolute structure parameters	–	–	0.01(3)
largest peak and hole [e Å^{-3}]	0.186, −0.201	0.151, −0.165	−0.287, −0.317

[a] Data in common: $\lambda = 0.71073$ nm, $T = 180(2)$ K, absorption correction, semiempirical from equivalents.

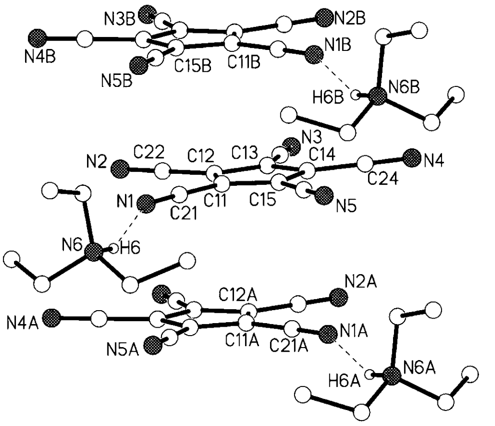


Figure 1. π Stacking, through a c glide, of H-bonded monomer units in the precursor $[Et_3NH][\mathbf{1}]$. Selected bond lengths [Å] and angles [°]; C≡N range 1.143(2)–1.150(2), C···C in C_5 ring range 1.404(2)–1.407(2), C–C (≡N) range 1.414(2)–1.423(2), N1···N6 3.015(2) [N6–H···N6 2.15(1), 154.9(1)], angle between the planes of C_5 rings 2.3, C_5···C_5 ca. 3.40 [C15···C21A 3.36].

between one of the ($\delta-$) C atoms of a C_5-ring and the ($\delta+$) C atoms of the C≡N groups of the two neighbouring anions [C15···C21A,21B 3.36 Å]; in-line with the fundamentally electrostatic nature of these interactions. The π stacking in $[Et_3NH][\mathbf{1}]$ is similar to that found in the lattice of the organic salts $[BEDT\text{-}TTF]_2[\mathbf{1}]$ [BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene], with C_5···C_5 inter-ring separation of 3.387(2) Å.[2a]

The structure of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ is built up from interlocked dimeric units of C_2 symmetry (Figure 2a), in which the $[C_5(CN)_5]^-$ ions coordinate the Na^+ ions in a side-on fashion using two adjacent 1,2-C≡N groups. Two further C≡N substituents [N3, N4] associate the dimer units into a complicated lattice arrangement (Figure 2b). Thus, the $[C_5(CN)_5]^-$ ligands act as a four-fold node, with the remaining C≡N group of each of the anions [N5] being involved in forming alternating −C≡N···C_5···−C≡N stacks within the lattice. These stacks are related by a 2_1 axis parallel to the crystallographic c axis, which result in α- and β-helical substructures linking the dimeric units (see Figure 2c). The closest C···C contact between adjacent C_5 rings in the stack [ca. 3.56 Å] is, however, slightly outside that expected for a van der Waal's interaction[10] and it is also noticable that the planes of neighbouring $[C_5(CN)_5]^-$ ions are distinctly pitched with respect to each other (by 13.7°). These probably constitute only weak π–π stacking interactions at the most. The structure is clearly dominated by the coordination demands of the Na^+ cations. The half occupancy of the symmetry related thf ligand sites [O2/O2A] (Figure 2a), results in both five- and six-coordinate Na^+ ions [Na1 and Na1A] being randomly distributed throughout the $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ lattice.

The structure of $[\{(tmeda)_2Na(\mathbf{1})\}_2]$ is found to contain dimeric molecules in which the $[C_5(CN)_5]^-$ ions bridge the Na^+ ions using two of the C≡N groups (Figure 3a). It is interesting to note the structural change in the dimer units from a 1,2-$(CN)_2$ linkage of the $[C_5(CN)_5]^-$ ions in the lattice of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ (Figure 2a) to a 1,3-$(CN)_2$ linkage in the discrete structure of $[\{(tmeda)_2Na(\mathbf{1})\}_2]$. The crystallographically independent octahedral $(tmeda)_2Na(N{\equiv}C\text{-})_2$ configurations at Na1 and Na2 are of opposite chirality. A further feature of the dimeric structure is the presence of two, short π–π C···C contacts between C38 in a ($\delta-$) C_5 ring of one anion and the ($\delta+$) C25 of a C≡N group of the other, across the metallocyclic cavity (see Figure 1b). These contacts [3.32–3.33 Å] are within the range anticipated for π–π interactions and are similar in origin to those found in $[Et_3NH][\mathbf{1}]$,[9] being electrostatic, between the positive and negative quadrants of the $[C_5(CN)_5]^-$ ion.

DFT calculations: DFT calculations (B3LYP/6-31G*)[11–13] on the $[C_5(CN)_5]^-$ ion reveal good agreement between the geometry-optimised structure and the experimentally observed anion geometries. The cyclopentadienyl C···C bond lengths [1.419 vs. 1.392(4)–1.415(4) Å] and exocyclic C–C bond lengths [1.417 vs. 1.414(2)–1.434(4) Å] as well as C≡N bonds [1.166 vs. 1.132(4)–1.148(4) Å] are all consistent with the dominant resonance form shown in Figure 4a and this was confirmed by an NBO analysis (Figure 4b, c). The fron-

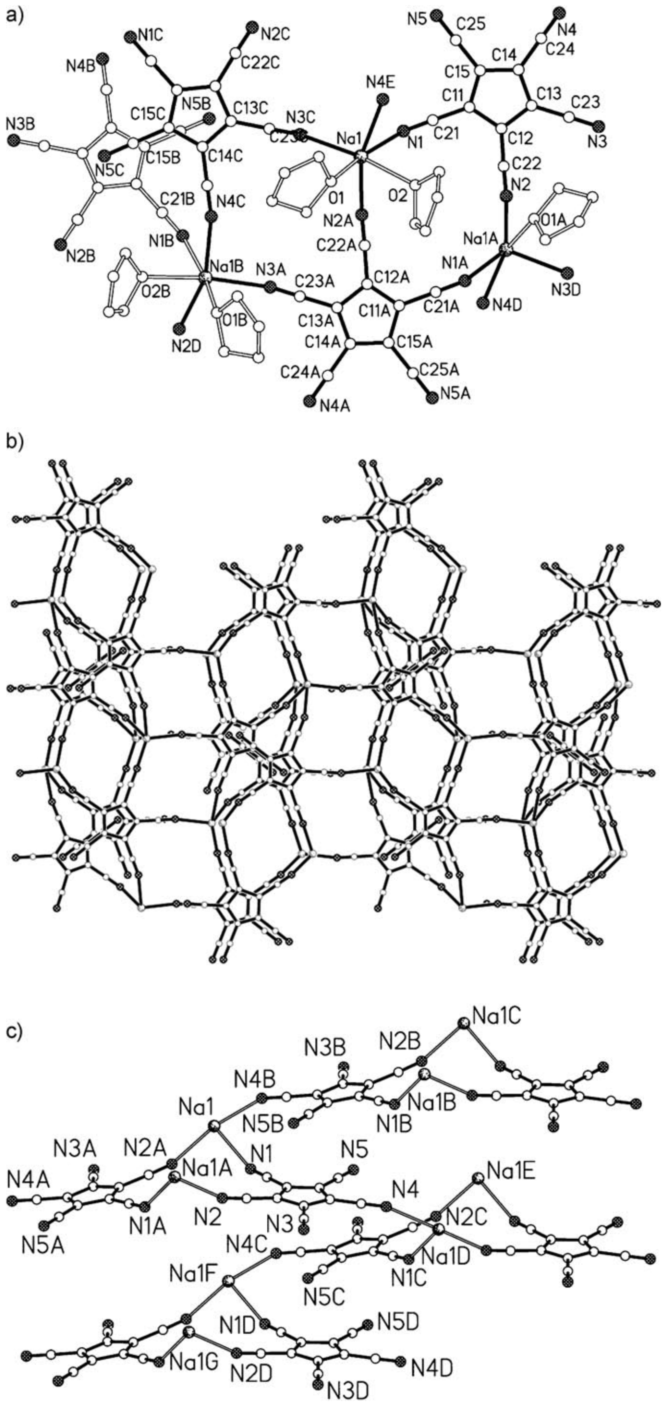


Figure 2. a) Dimeric, metallocyclic building blocks of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$, showing 5- and 6-coordination at Na1 and Na1a, respectively, caused by the 50:50 disorder of the thf sites. Selected bond lengths [Å] and angles [°]: Na1–N1 2.496(3), Na1–N2A 2.455(3), Na1–N3B 2.422(3), Na1–N4C 2.472(3), Na1–O1 2.361(3), Na–O2 2.490(5), C≡N range 1.137(4)–1.148(4), C⋯C in C_5 ring range 1.400(4)–1.410(4), C–C(≡N) range 1.422(4)–1.428(4), N1-Na1-Na2A 88.2(1), range of angles about Na1 77.1(1)–168.7(1). b) Bonding of these units into a 3D lattice (viewed down the crystallographic *a* axis). c) Formation of helical segments by the assocation of dimer units which interdigitate into C≡N⋯C_5 stacks (thf solvation of the Na^+ ions is omitted for clarity).

tier orbitals of the anion are analogous to those for the $C_5H_5^-$ ion (see the Supporting Information).

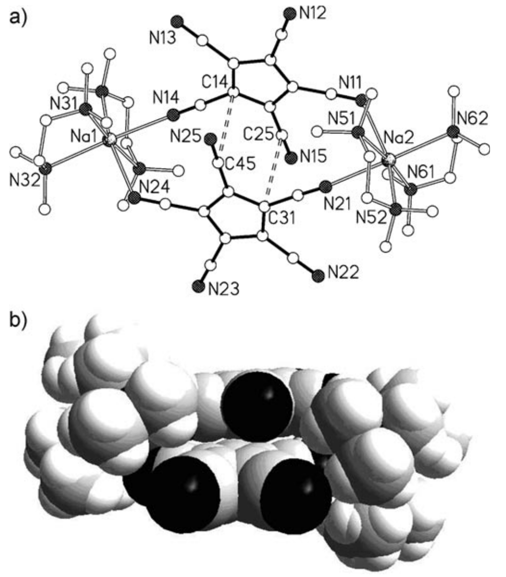


Figure 3. a) Metallocyclic structure of dimers of $[\{(tmeda)_2Na(\mathbf{1})\}_2]$. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Na1–N14 2.500(3), Na1–N24 2.765(3), Na2–N11 2.731(3), Na2–N21 2.516(2), C≡N range 1.132(4)–1.148(4), C⋯C in C_5 ring range 1.392(4)–1.415(4), C–C(≡N) range 1.419(4)–1.434(4), N21-Na2-N11 81.92(9), N14-Na1-N24 81.28(9). b) Space-filling representation of view parallel to the C_5 rings of the bridging anions; rings are parallel within 2.3°, closest C⋯C [C31⋯C25/C14⋯C45] interactions 3.32–3.33 Å.

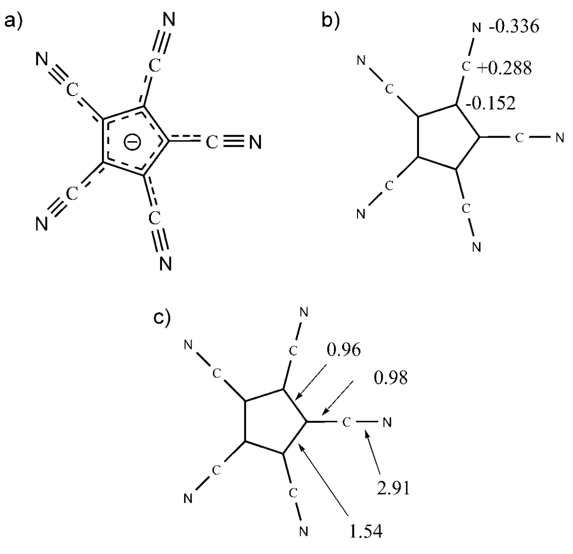


Figure 4. a) Principal resonance form, b) charges and c) bond orders calculated in the $[C_5(CN)_5]^-$ ion.

Understandably, the negative charge on the C_5-ring unit of the $[C_5(CN)_5]^-$ ion is dispersed towards the C≡N groups, reducing the negative charge carried by the ring carbon atoms compared to the $C_5H_5^-$ ion (from −0.38e in $C_5H_5^-$ to −0.15e in $[C_5(CN)_5]^-$). This relatively low negative charge on the ring carbon atoms and the large negative charge on the C≡N N atoms in $[C_5(CN)_5]^-$ (−0.34e) results in a more favourable σ-type interaction with a Na^+ ion in the monomer (Figure 5a), which is 31 kJmol^{-1} more stable than a π-type interaction (Figure 5b).

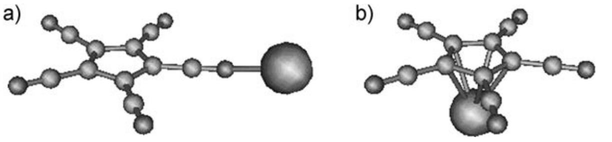
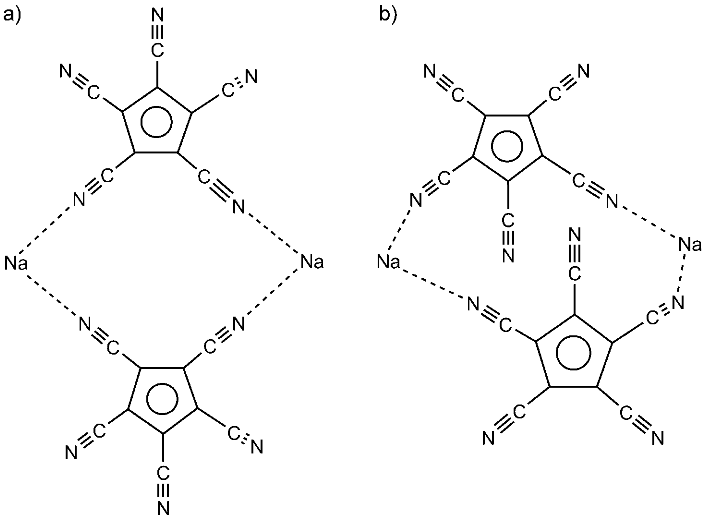


Figure 5. a) σ-Type and b) π-type interaction of a Na$^+$ ion with the $[C_5(CN)_5]^-$ ion.

Two dimerisation models were considered involving a 1,2-linkage of the $[C_5(CN)_5]^-$ anions (Figure 5a) [as occurs in the dimer units of the lattice of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$] and a 1,3-linkage (Scheme 3b) (found in the dimer $[\{(tmeda)_2Na(\mathbf{1})\}_2]$). Dimerisation from the σ-bonded monomer (Scheme 3a) to the 1,2-linked dimer (Scheme 3a) is favoured by 225 kJ mol^{-1}, whereas dimerisation to the 1,3-dimer is favoured by 234 kJ mol^{-1} (making the 1,3-dimer slightly more favourable than the 1,2-dimer by 9 kJ mol^{-1}). It can be noted also that the dimerisation of two *separate* $[C_5(CN)_5]^-$ ions with a similar orientation to that found in the dimer $[\{(tmeda)_2Na(\mathbf{1})\}_2]$ is unfavourable by 197 kJ mol^{-1}, suggesting that if present the inter-ring π–π interactions are weak and that the formation of this dimer is dominated by the coordination requirements of the Na$^+$ ions. The fact that there is only a small energy separation between the 1,2- and 1.3-dimers is consistent with the observation of these modes in the structures of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and $[\{(tmeda)_2Na(\mathbf{1})\}_2]$, the balance between them being highly likely to be influences by the type and extent of solvation of the Na$^+$ ions.



Scheme 3. a) 1,2-Linked dimer and b) the 1,3-linked dimer.

Conclusion

We have found a very simple way to access (in theory) any metal salt of the $[C_5(CN)_5]^-$ ion and we have applied this methodology to the sodium compounds in this study. The single-crystal studies of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and $[\{(tmeda)_2Na(\mathbf{1})\}_2]$ are the first undertaken on any metal compounds containing this ligand.[14] Not surprisingly, the $[C_5(CN)_5]^-$ ion exhibits a marked tendency for σ-C≡N bonding over C_5-π bonding, owing to charge dispersion to the C≡N groups. This leads to distinctly different structures from all of the previously reported sodium cyclopendienide counterparts, in which π-bonding dominates, a case in point being a comparison between the highly complicated 3D structure of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ and the 2D, π-bonded polymer arrangement found in the cyclopentadienide sodium complex $[CpNa{\cdot}thf]_\infty$.[3c]

Experimental Section

All experiments were undertaken under a dry argon atmosphere on a vacuum-line in Schlenk tubes using inert-atmosphere techniques. A glove-box (Saffron, type b) was used to store and isolate products and reactants, to weigh out air-sensitive and hygroscopic solid materials and to prepare analytical samples. Et_3NHCl (used in the preparation of $[Et_3N][\mathbf{1}]$) was acquired from Aldrich Chemical Company and used as supplied. All solvents were dried by distillation before use. A Perkin–Elmer 1710 spectrophotomer was used to obtain IR spectra on Nujol mulls. Elemental C,H,N analysis was performed by using a Perkin–Elmer 240 elemental analyser. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer.

The anion **1** was prepared by using the previously reported synthesis, and was precipitated by the addition of Et_3NHCl.[7] ^{1}H NMR (500.05 MHz, $[D_6]$DMSO, +25 °C): δ=8.82 (brs., 1H), 3.29 (s, 6H), 3.07 (q, $^1J_{H,H}$=7.2 Hz), 1.15 ppm (t, 9H, $^1J_{H,H}$=7.2 Hz); ^{13}C NMR (125.75 MHz, $[D_6]$DMSO, +25 °C): δ=113.5 (C≡N of **1**), 102.2 (C_5 ring of **1**), 46.2 (CH_2), 9.1 ppm (CH_3); elemental analysis calcd (%) for $[Et_3NH][\mathbf{1}]$: C 65.7, H 5.5, N 28.8; found: C 65.1, H 5.4, N 28.3.

Synthesis of $[Na(thf)_{1.5}(\mathbf{1})]_\infty$: NaH (60 % dispersion in mineral oil, 10 mg, 0.25 mmol) was added to a solution of $[Et_3NH][\mathbf{1}]$ (20 mg, 0.07 mmol) in thf (10 mL) at room temperature and the mixture stirred overnight. The solution was reduced in volume to about 1 mL by rotary evaporation and then filtered through a plug of Celite filter agent into a 1 cm wide test tube placed in a Schlenk tube containing n-pentane (5 mL). The Schlenk tube was stoppered and left undisturbed for several days during which time colourless plates had formed. The solvent liquor was removed by using a syringe and the crystals collected and dried in vacuo. Yield 12 mg (80 %). ^{13}C NMR (125.75 MHz, $[D_6]$DMSO, +25 °C): δ=113.1 (C≡N), 101.8 ppm (C_5 ring); elemental analysis calcd (%) for $[Na(\mathbf{1})]$: C 56.4, H 0.0, N 32.9; found: C 55.8, H 0.25, N 32.1 (showing that the thf solvation is almost completely removed by placing the sample under vacuum during isolation).

Synthesis of $[\{(tmeda)_2Na(\mathbf{1})\}_2]$: The same method and quantities were used as for $[Na(thf)_{1.5}(\mathbf{1})]_\infty$ except crystallisation was effected by layering 5 mL tmeda directly onto a 1 mL thf solution in a 0.5 cm wide test tube. After several days, needle-shaped crystals had formed. The solvent liquor was removed via syringe and the crystals dried by blowing Ar over them for 2 h. Yield 11 mg (35 %). ^{1}H NMR (500.05 MHz, $[D_6]$DMSO, +25 °C): δ=2.25 (s, 4H, -CH_2-, tmeda), 2.10 ppm (s, 12H, CH_3, tmeda); ^{13}C NMR (125.75 MHz, $[D_6]$DMSO, +25 °C): δ=113.1 (C≡N of **1**), 101.8 (C_5 ring of **1**), 57.3 (-CH_2-, tmeda), 45.6 ppm (CH_3, tmeda); elemental analysis calcd (%) for $[\{(tmeda)_2Na(\mathbf{1})\}_2]$, C 59.3, H 7.2, N 28.3; found: C 57.9, H 6.0, N 27.7. The elemental analysis results indicate that up to approximately 0.5 of a tmeda ligand is lost from the complex upon isolation under vacuum.

X-ray crystallographic studies on [Et_3NH][1], [$Na(thf)_{1.5}$(1)]$_\infty$ and [{$(tmeda)_2Na$(1)}$_2$]: Crystals of the compound were mounted directly from solution using perfluorocarbon oil.[15] A Nonius KappaCCD diffractomer was used for all data collections. Data was solved by direct methods and refined by full-matrix least squares on F^2.[16] CCDC-783704 ([Et_3NH][**1**]), CCDC-783705 ([$Na(thf)_{1.5}$(**1**)]$_\infty$) and CCDC-783706 ([{$(tmeda)_2Na$(**1**)}$_2$]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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