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Synthesis and Properties of a New Chelating Ligand, 4,7-Bis(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline

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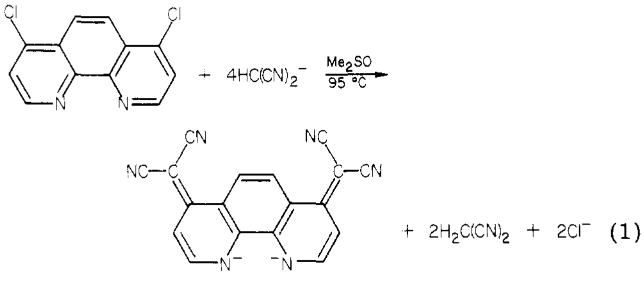
The synthesis and properties of the compound 4,7-bis(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline, as the dianion, $C_{18}H_6N_6^{2-}$, and its complexes with Na^+ and Li^+ are reported. This compound can be viewed as a derivative of the chelating ligand 1,10-phenanthroline but differs substantially in its electronic structure and chemical properties. The conversion of the $C_{18}H_6N_6^{2-}$ dianion to the fully protonated parent compound $C_{18}H_8N_6$ and its isolation as an adduct with 18-crown-6 are also described.

Introduction

The compound 1,10-phenanthroline and its close relative 2,2′-bipyridine have been widely used as chelating bidentate ligands in coordination chemistry and their ruthenium(II) complexes in particular have been of much interest in connection with the conversion of light into chemical energy.[1] In the course of studies directed at optimizing the photophysical characteristics of such ruthenium(II) complexes through structural modification of the 1,10-phenanthroline ligand system, we have prepared a new ligand system whose electronic, structural, and coordination properties differ considerably from those of the parent 1,10-phenanthroline system. We report here the synthesis and propertis of this new compound, 4,7-bis(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline, as he dianion, $C_{18}H_6N_6^{2-}$ (1), in complexes with Na^+ and Li^+ and in the neutral protonated form, $C_{18}H_8N_6$, as an adduct with 18-crown-6.

Results and Discussion

The reaction of 4,7-dichloro-1,10-phenanthroline with excess $NaHC(CN)_2$ in Me_2SO at 95 °C proceeds smoothly according to eq 1 to form 4,7-bis(dicyanomethylidene)-1,4,7,10-tetrahydro-1,10-phenanthroline as the dianion, $C_{18}H_6H_6^{2-}$ (1). The mechanism likely involves nucleophilic displacement of Cl^- by $HC(CN)_2^-$ followed by proton abstraction by excess $HC(CN)_2^-$.[2,3] The yellow-orange solid obtained after removal of Me_2SO and treatment with water has an ill-defined stoichiometry but shows infrared and NMR features characteristic of 1 (vide infra). Attempted recrystallization from acetonitrile or ethanol/water was ineffective. Solubility in other solvents tested was too low to be useful. The material is also insoluble in inorganic acids and any aqueous base solution containing metal ions. Both the solid and its lightly colored aqueous solutions show changes in hue with pH, indicating that 1 has acid-base properties. Similar color changes with pH were noted in the purified compounds described below.



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A well-defined material containing 1 was obtained by dissolving the solid in a 10% tetraethylammonium hydroxide solution and then adding a solution of an alkali metal or alkaline earth salt. Although precipitates were obtained for all ions tried, only the Na^+ and Li^+ products have been fully characterized as the mixed cation salts $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$ and $[(C_2H_5)_4N]Li(C_{18}H_6N_6)$. Well-formed yellow plates of both compounds are obtained on crystallization from CH_3CN/Et_2O. The crystals can be handled conveniently in air but contact with moisture causes a surface color change to orange.

Major spectroscopic features of the Li^+ and Na^+ salts are summarized in Table I. The two strong C≡N stretching bands are characteristic of the $=C(CN)_2$ group.[4] The pair of doublets (J = 5–6 Hz) and one singlet of relative areas 1:1:1 in the ^1H NMR spectrum are as required for structure 1. Assignment of the lower field doublet to the 2,9 protons is based on the large downfield shift of this resonance compared to the higher field doublet on coordination to ruthenium(II).[5] This pattern is typical of the 2,9 and 3,8 resonances in 1,10-phenanthroline related ligands.[6]

The strong affinity of 1 for metal ions, even alkali metals, was unexpected and suggests that it forms coordination complexes rather than simple ionic salts. Alkali-metal complexes of neutral chelating nitrogen-donor ligands, including 1,10-phenanthroline, are well-known but are, in general, not stable in aqueous solution.[7] The donor ability of the dianion 1 toward such metal ions should be enhanced due to the formal negative charge on the nitrogen atoms. The exceptional affinity of the $C_{18}H_6N_6^{2-}$ ion for even alkali-metal ions is illustrated by the results of efforts to isolate the fully protonated derivative, $C_{18}H_8N_6$. Acidification of solutions of $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$ dissolved in ethanol/water or tetraethylammonium hydroxide gave nonstoichiometric solids which retained sodium and, in the latter system, $(C_2H_5)_4N^+$. Treatment of the crude product originally precipitated from Me_2SO by prolonged stirring in concentrated hydrochloric acid also was unsuccessful. However, treatment of a 4:1 ethanol/

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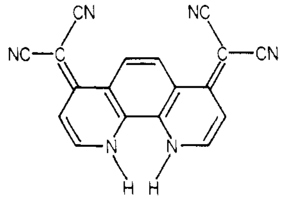
Table I. Selected Infrared and NMR Assignments for $C_{18}H_6N_6^{2-}$ in Its Compounds

	IR, cm^{-1} [a]		NMR shifts [b]			
compd	ν (C≡N)	ν (NH)	$H_{2,9}$	$H_{3,8}$	$H_{5,6}$	NH
$[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$	2135, 2175		8.31 (d)	6.93 (d)	8.47 (s)	
$[(C_2H_5)_4N]Li(C_{18}H_6N_6)$	2135, 2175		8.31 (d) [c]	7.03 (d) [c]	8.62 (s) [c]	
$(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)\cdot 3H_2O$	2180, 2196	3150, 3240	8.21 (d)	7.02 (d)	8.61 (s)	~9.3 (br)

[a] Nujol mull. [b] δ values to internal Me_4Si in Me_2SO-d_6; d = doublet, s = singlet, br = broad. [c] In CD_3CN.

water solution of this crude material with excess 18-crown-6 ($C_{12}H_{24}O_6$) followed by addition of aqueous hydrochloric acid gave fine crystals of the yellow, sodium-free compound $(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)\cdot 3H_2O$. That protonation occurs to give 2 and not 3 is supported by spectroscopic data. Two new infrared features at 3150 and 3240 cm^{-1} indicate the presence of NH protons. A new broad peak in the ^1H NMR spectrum at δ ~9.3 is also consistent with NH protons; the proton on a $CH(CN)_2$ group is expected to give a relatively sharp peak in the δ 5–6 range.[4]



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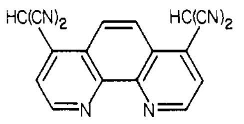

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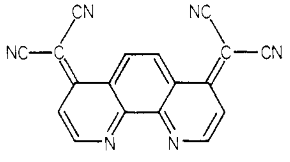
This conclusion is also supported by the preliminary results of a ^{13}C NMR study of the protonated species as its 18-crown-6 adduct, $(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)\cdot 3H_2O$.[8] The ^{13}C spectrum of this compound shows no indication of any ^{13}C peaks in the aliphatic carbon region between 0 and 110 ppm other than those attributable to 18-crown-6 and the solvent, Me_2SO.

The incorporation of 18-crown-6 in $(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)\cdot 3H_2O$ was unexpected but probably arises because of hydrogen bonding between the NH protons of 2 and the 18-crown-6 oxygen atoms. Such hydrogen bonding has been found in other compounds between crown ethers and molecules with acidic CH,[9,10] OH,[11] or NH[12] protons. The compound shows none of the infrared features characteristic of a crown ether–H_3O^+ complex as occurs in the dicyclohexyl-18-crown-6 complexes of $HClO_4$ and HPF_6.[13] Hence we rule out a formulation with one $C_{18}H_7N_6^-$ and an H_3O^+/18-crown-6 complex, $(C_{18}H_8N_6)(C_{18}H_7N_6)[(H_3O)(C_{12}H_{24}O_6)]\cdot 2H_2O$. Although this is viewed as unlikely, an 18-crown-6 complex with a more highly hydrated proton than H_3O^+ cannot be excluded.

It was anticipated that two-electron oxidation of 1 would provide the neutral 4,7-substituted 1,10-phenanthroline, 4. Cyclic volammetry of 1 in acetonitrile does show two oxidation waves at +0.47 and +0.66 V vs. SCE, but the processes are irreversible (see Figure 1). This contrasts with 1,10-phenanthroline, which shows no oxidation up to +2.1 V but is reduced irreversibly at −2.1 V vs. SCE.[14] The effect of introducing the two strong electron withdrawing groups at the 4 and 7 positions of the phenanthroline ring strongly stabilizes the reduced form of the ligand. Because of its apparent instability, we have made no attempt to isolate the oxidation product.



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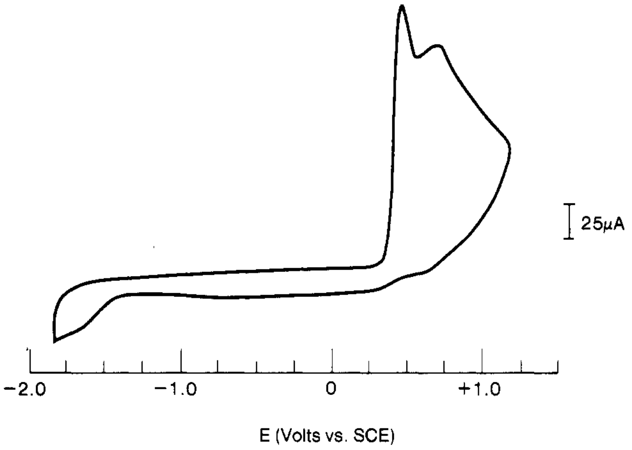

Figure 1.

Finally, we would like to note that the electronic structures of the unoxidized ligand, 1, and 1,10-phenanthroline are basically quite different. In 1,10-phenanthroline the two nitrogen-containing rings have aromatic character and are connected by a relatively normal double bond at the 5 and 6 carbon atoms,[15] whereas in 1 the nitrogen-containing rings are nonaromatic, while the central C_6 ring should have a benzene-like π-electronic structure. These differences in π-electronic structure and in the formal negative charge on the nitrogen atoms suggest that the properties of 1 and 1,10-phenanthroline as ligands in metal complexes should be quite different in many respects, particularly where the π-electron system of the ligand is concerned. Preliminary results on the ruthenium(II) complexes of 1[5] as well as the results reported here on the Na^+ and Li^+ compounds tend to support this conclusion.

Experimental Section

Dimethyl sulfoxide (Me_2SO) was dried over and distilled from CaH_2 at reduced pressure (~8 torr, bp 58 °C) and stored over 4-Å molecular sieves under nitrogen. Acetonitrile for cyclic voltammetry was dried over 3-Å molecular sieves for at least a week, distilled from CaH_2 under nitrogen, and stored in a glovebox.[16] Malononitrile was recrystallized from diethyl ether and ferrocene was freshly sublimed. Electrolytic grade tetrabutylammonium fluoroborate (Southwestern Analytical Chemi-

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cals, Inc.) was dried overnight at 135 °C under vacuum before use. 4,7-Dihydroxy-1,10-phenanthroline was purchased from G. F. Smith. All other chemicals were used as received from commercial sources.

Elemental analyses were performed in the General Electric CR&D Microanalytical Laboratory. NMR spectra were recorded on a Varian FT80 spectrometer.

$[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$. The first phase of the reaction was carried out under nitrogen with dried solvents. A 1.58-g sample of sodium hydride (56.9% NaH, 39.3 mmol) was washed with petroleum ether to remove mineral oil and dried. After addition of 40 mL of Me_2SO, 3.29 g (49.9 mmol) of malononitrile was added in small portions with stirring. Finally, 1.58 g (6.36 mmol) of 4,7-dichloro-1,10-phenanthroline[17] was added and the solution volume increased to about 90 mL with Me_2SO. The mixture was heated at 90–95 °C for 16 h to give a deep-yellow solution. After the mixture was cooled to room temperature, the reaction was quenched with ~1 mL of H_2O and the Me_2SO removed under reduced pressure with a dry-ice condenser. This and subsequent operations were done in air. The solid residue was treated with 150 mL of H_2O, filtered, washed extensively with H_2O, and dried under vacuum at 80 °C: yield, 2.99 g; yellow-orange powder.

About 1.7 g of the crude product was dissolved in ~400 mL of 10% tetraethylammonium hydroxide solution. An insoluble residue was filtered off, and the filtrate was treated dropwise with 50% NaOH until precipitation ceased (~10 mL). The crude $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$ was collected and washed with a small portion of $(C_2H_5)_4NOH$ solution. Drying as above gave 1.56 g (1.52 mmol) of product or 85% based on the initial 4,7-dichloro-1,10-phenanthroline. This crude salt was taken into a minimum quantity of warm acetonitrile and any residue filtered off. The solution was warmed and the volume reduced to nearly cause precipitation followed by ether addition to the cloud point. Cooling to −20 °C gave clear yellow platelets, which were filtered and washed with cold 1:1 acetonitrile/ether. The cold crystals should be protected from moisture which turns them orange. The product was dried at 110 °C under vacuum. Several crops gave a total of 1.25 g (1.22 mmol, 68% overall yield). Anal. Calcd for $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$: C, 70.2; H, 7.1; N, 20.5; Na, 2.2. Found: C, 70.1; H, 7.2; N, 20.5; Na, 2.2. Absorption spectrum (CH_3CN) 213 nm (log ϵ 5.39), 250 (4.43), 273 (4.35), 391 (4.51), 411 (4.57).

$[(C_2H_5)_4N]Li(C_{18}H_6N_6)$. The crude solid was obtained from tetraethylammonium hydroxide solution as above by addition of aqueous lithium chloride. Initially an oil formed which solidified on standing and was then filtered. A sample of 102 mg of initial reaction product gave 100 mg of crude $[(C_2H_5)_4N]Li(C_{18}H_6N_6)$. Recrystallization by slow addition of twice the volume of ether to a concentrated acetonitrile solution at 0 °C gave 60 mg of pure $[(C_2H_5)_4N]Li(C_{18}H_6N_6)$. Anal. Calcd: C, 70.4; H, 5.9; N, 22.1. Found: C, 70.0; H, 6.2; N, 22.1.

Metal-Free $C_{18}H_8N_6$. A 100-mg sample of the orange-yellow solid from the $HC(CN)_2^-$/4,7-dichloro-1,10-phenanthroline reaction was dissolved in 50 mL of 4:1 ethanol/water with warming followed after filtration by addition of 1.5 g of 18-crown-6 and 1.0 mL of 12 M HCl to the warm solution. The mass of fine yellow-orange crystals which formed on cooling to room temperature was collected by filtration, washed several times with ethanol containing 1 mL of 12 M HCl per 75 mL, and air-dried: yield, 91 mg. Anal. Calcd for $(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)\cdot 3H_2O$: C, 61.7; H, 5.0; N, 18.0. Found: C, 61.7; H, 4.8; N, 18.4 A flame test for Na was negative.

Cyclic voltammetry was performed with a Pine Instruments Co. Model AFRDE3 potentiostat and a Hewlett-Packard 7034A X-Y recorder. The electrochemical cell consisted of three compartments separated by glass frits; the center compartment was used for the working electrode. The working and counter electrodes were platinum wires, and the reference electrode was a silver wire. The electrodes were inserted through rubber septa which were used to seal the top of each cell compartment. The cell, electrodes, and all other glassware were dried at 140 °C overnight and transferred to an argon-filled Vacuum Atmospheres glovebox for solution preparation while still hot. The cell was charged with freshly prepared 0.1 M $(n\text{-}C_4H_9)_4NBF_4$/acetonitrile solution. This electrolyte solution was also used to prepare a sample solution and a ferrocene solution in separate containers which were also sealed with rubber septa. Following preliminary scans of the electrolyte solution, the sample solution was added by using standard transfer techniques for oxygen and moisture-sensitive materials and mixed with the aid of a magnetic stir bar. When measurements on the sample were completed, the ferrocene standard was added, and further spectra were recorded for voltage calibration.[18]

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Registry No. $[(C_2H_5)_4N]_3Na(C_{18}H_6N_6)_2$, 81315-62-0; $[(C_2H_5)_4N]Li(C_{18}H_6N_6)$, 81315-63-1; $(C_{18}H_8N_6)_2(C_{12}H_{24}O_6)$, 81315-65-3; malononitrile, 109-77-3; 4,7-dichloro-1,10-phenanthroline, 5394-23-0.

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Intramolecular Cyclization of Peri-Substituted 1-Azidonaphthalenes. 3.[1] Structural and Chemical Investigation of 1-(Arylamino)benz[*cd*]indazol-8(and -6)(1*H*)-ones Produced by Decomposition of Hydroxy-Substituted 8-Azido-1-(arylazo)naphthalenes

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Thermal and photochemical decomposition of 8-azido-2-hydroxy-1-(arylazo)naphthalenes **3a–d** leads to 1-(arylamino)benz[*cd*]indazol-8(1*H*)-ones **4a–d** in good yields. Analogous results are obtained in the conversion of **5** into **6**. The reactions appear to proceed through 1,5-cyclization of the tautomeric hydrazone forms of the azides, and the absence of products that would be expected from nitrene intermediates suggests that the reactions proceed through a concerted mechanism. Evidence is presented to support the benzindazolone structures rather than the isomeric triazines. The ratios of *O*- and *N*-alkyl derivatives obtained on alkylation of **4a–d** depend on the type of substituent in the arylamino ring and on the bulk of the alkyl group.

The thermal and photochemical decomposition of 8-azido-1-(arylazo)naphthalenes (**1**, R = H or OCH_3) have been shown to lead to the corresponding benz[*cd*]indazole *N*-aryl imines **2**, apparently through a concerted cyclization

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