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Charge transfer in the viologen (1,1′-dialkyl-4,4′-bipyridinium ion) salts of cyanocuprate(I)

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Abstract

The viologen salts of cyanocuprate(I), $HV^{2+}[Cu(CN)_3]^{2-}\cdot 2H_2O$ and $MV^{2+}[Cu_3(CN)_5]^{2-}$ (HV^{2+} = 1,1′-diheptyl-4,4′-bipyridinium ion; MV^{2+} = 1,1′-dimethyl-4,4′-bipyridinium ion), were obtained by mixing a solution of the appropriate alkylviologen halide with a solution containing CuCN and NaCN. The resulting red–brown materials exhibited charge-transfer bands with maxima at 370 and 500 nm in the solid state, and at 350 nm in aqueous solution. The presence of Cu^I ions and viologen dications was deduced from the X-ray photoelectron spectra of the solid compounds. An X-ray crystal analysis of $HV[Cu(CN)_3]\cdot 2H_2O$ showed that a copper atom was located on a triangular plane formed by three CN carbon atoms. A $[Cu(CN)_3]^{2-}$ ion and an HV^{2+} ion were stacked face-to-face to form an ion pair with a close Cu–C contact of 3.2 Å. This Cu–C contact is responsible for the cation–anion charge transfer. The ion pairs are so stable that the charge-transfer bands are found even in solution.

Introduction

A viologen (1,1′-dialkyl-4,4′-bipyridinium ion) salt has a variety of novel applications: for example, it is an electron transfer inhibitor, a redox indicator in biological systems and even a herbicide [1]. These applications are based on the high stability of the doubly-charged cation, its low reduction potential to a radical cation and a high charge-transfer capacity. Recent interest in viologens has been also directed to their use as materials for the synthesis of organic conductors and the fabrication of electronic devices such as electrochromic and/or photochromic memory displays [2–6]. These applications are related to the sensitive color changes that are caused by either a charge-transfer or redox reaction.

A variety of metal complex anions have been reported to form viologen salts [7–14]. The advantage in the use of metal complexes as counteranions is the flexibility in the molecular design of viologen complexes, because different types of metal complex anions can be readily obtained by appropriate combinations of central metals and coordinated ligands. The use of anionic copper complexes as counterions is expected to yield interesting viologen compounds, because the potential for the reduction of the complexed copper(II) to the copper(I) state is relatively small. It has been reported that methylviologen forms intensely colored complexes with halocuprate(II) anions [7–9, 13]. An absorption band that arises from a charge transfer between copper and viologen was, however, not detected; the color was attributed, instead, to a charge transfer within the halocuprate ion [7]. The electron-donating capacity of a metal complex anion is strongly dependent on the coordinated ligand and the oxidation state of the central metal. A copper atom in the Cu^I state, therefore, is expected to have a higher electron-donating ability to a viologen(2+) cation, than a copper atom in the Cu^{II} state. We have studied reactions between cyanocuprate(I) anions and viologen cations in the present work, and obtained a red–brown complex of heptylviologen (1,1′-diheptyl-4,4′-bipyridinium, abbreviated as HV^{2+}), $HV[Cu(CN)_3]\cdot 2H_2O$, and a light brown methylviologen complex, $MV[Cu_3(CN)_5]$. An X-ray crystal analysis of the HV complex was carried out and it was found that an HV^{2+} and a $[Cu(CN)_3]^{2-}$ form an

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ion pair with a close Cu–C contact, through which the charge transfer occurs.

Experimental

Heptylviologen(2+) bromide and methylviologen(2+) chloride hydrate supplied from Aldrich Chemical Co. were used without further purification.

HV[$Cu(CN)_3$]·$2H_2O$ was obtained as a reddish brown powder when an aqueous solution (40 ml) containing NaCN (47.6 mg) and CuCN (43.5 mg) was added dropwise to heptylviologen bromide (500 mg) in water (10 ml). The product was washed with water and dried in vacuum. *Anal.* Calc. for $C_{27}H_{42}N_5O_2Cu$: C, 60.93; H, 7.96; N, 13.16; Cu, 11.94. Found: C, 61.06; H, 7.91; N, 13.26; Cu, 11.92%. Single crystals were grown by diffusing together $[Cu(CN)_3]^{2-}$ and HV^{2+} in a double-wall cell: an aqueous heptylviologen bromide solution was placed in the inner tube, and an aqueous solution containing KCN (or NaCN) and CuCN in a 2:1 ratio was loaded in the outer tube. In a month, red–brown crystals with well-defined faces were formed.

MV[$Cu_3(CN)_5$] was prepared by adding an aqueous solution (40 ml) containing NaCN (95.2 mg) and CuCN (174 mg) to an aqueous solution (10 ml) of methylviologen chloride hydrate (500 mg). The light brown powder obtained was washed with water and dried in vacuum. *Anal.* Calc. for $C_{17}H_{14}N_7Cu_3$: C, 40.27; H, 2.78; N, 19.34; Cu, 37.6. Found: C, 40.96; H, 2.73; N, 19.04; Cu, 35.9%.

The C, H and N analyses were performed by Desert Analytics, Tucson, AZ, USA, and the Cu content was determined by EDTA titration.

The X-ray reflections were collected on an HV[$Cu(CN)_3$]·$2H_2O$ crystal with approximate dimensions of 0.33×0.13×0.08 mm on a Syntex $P2_1$ diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The space group was $P\bar{1}$. The cell parameters and the calculated cell volume were: $a = 16.920(8)$, $b = 19.040(9)$, $c = 9.461(4)$ Å, $\alpha = 97.990(4)$, $\beta = 99.109(4)$, $\gamma = 99.236(5)°$ and $V = 2927.90$ Å^3. For $Z = 4$ with two independent HV[$Cu(CN)_3$]·$2H_2O$ molecules per asymmetric unit and molecular weight = 532.2 of $C_{27}H_{42}N_5O_2Cu$, the calculated density was 1.207 g cm^{-3}. $F(000)$ was 1136. The data were collected in the range $0 < 2\theta \leqslant 35°$ at a temperature of 23 °C. A total of 3894 reflections was collected, of which 3703 were unique. No absorption corrections were made. The structure was solved by direct methods, and was refined with a full-matrix least-squares method by using 1417 reflections that had intensities greater than 3 times their standard deviations. Five carbon atoms in each heptyl group were highly disordered and included in the refinement with reasonable thermal parameters and fractional occupancies. Anisotropic refinement was not carried out except for copper, and hydrogen atoms were not included in the refinement. The final agreement factors were: $R = 0.09$ and $R_w = 0.11$. These large R values were due to the disorder of heptyl groups.

The X-ray photoelectron spectra (XPS) were obtained on a compressed pellet with the aid of an ESCALAB MK II spectrometer (East Grinstead, UK) with a Mg Kα X-ray source (1253.6 eV). There was no indication of sample decomposition during the X-ray irradiation. The binding energies were calculated by using the carbon 1s peak as an internal standard: its peak maximum was assumed to have a binding energy of 284.6 eV.

The electronic absorption spectra were obtained with a Perkin-Elmer Lambda 2 UV–Vis spectrometer. The IR spectra were recorded with a Perkin-Elmer 1420 spectrometer in KBr pellets and Nujol mulls; it was confirmed that the spectrum was not dependent on the sample preparation conditions.

Results

Heptylviologen (HV^{2+}) salt

When an aqueous solution of heptylviologen(2+) bromide was mixed with an aqueous solution containing CuCN and NaCN in the molar ratios, NaCN/CuCN = 2 and 3, HV[$Cu(CN)_3$]·$2H_2O$ was obtained as a reddish brown crystalline powder, independent of the NaCN/CuCN ratio. For NaCN/CuCN = 1, a light brown powder was obtained, but its composition could not be established. In the X-ray photoelectron spectrum (XPS) of HV[$Cu(CN)_3$]·$2H_2O$, a $2p_{3/2}$ core-electron peak of copper was observed at a binding energy of 932.5 eV with a full width at half maximum (FWHM) of 2.8 eV, and a $2p_{1/2}$ peak at 952.7 eV with an FWHM of 3.4 eV, as shown in Fig. 1. These binding energies are reasonable for Cu^I species [15]. Moreover, the peaks were not accompanied by shake-up satellites that are charac-

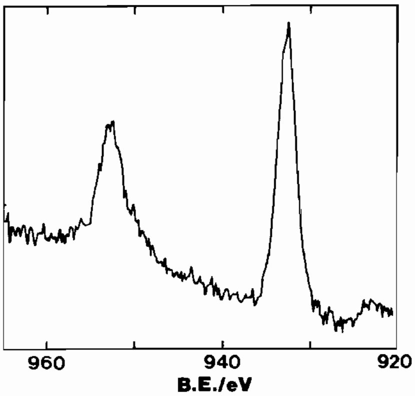


Fig. 1. X-ray photoelectron peaks observed for the $2p_{1/2}$ and $2p_{3/2}$ core electrons of copper in HV[$Cu(CN)_3$]·$2H_2O$.

teristic of Cu^{II} species. The copper atoms are, therefore, in the Cu^{I} oxidation state. The 1s core-electron spectrum of nitrogen consisted of two component peaks as shown in Fig. 2. The peak at a binding energy of 397.5 eV can be attributed to the negatively charged nitrogen of CN^-, and the peak at 400.9 eV to the positively charged nitrogen of viologen. The ratio of the N^- peak area with respect to the N^+ area was approximately 3:2, in agreement with the composition determined by the elemental analyses. These XPS results indicate that the compound formula is: $HV^{2+}[Cu^{I}(CN)_3]^{2-}$. No redox reaction occurred between HV^{2+} and Cu^{I} ions, and paramagnetic species such as Cu^{II} ions or $HV^{+\bullet}$ cation radicals were not involved. This conclusion was supported by the absence of an electron paramagnetic resonance signal for this compound.

Figure 3 shows the crystal packing in the unit cell. The positional parameters of non-hydrogen atoms are shown in Table 1. In the heptyl groups, the carbon atoms, except those bonded to nitrogen (C21, C31, C41 and C51), were disordered. The carbon atoms C22, C32, C42 and C52 showed very large thermal parameters due to disorder. The other carbon atoms could not be located with certainty, and their atomic coordinates are, therefore, not included in Table 1. Interatomic distances and bond angles are collected in Table 2 and 3, respectively. A copper atom is located on a triangular plane formed by three cyanide carbon atoms. The resulting $[Cu(CN)_3]^{2-}$ units are not linked with each other by a cyano ligand. The 'discrete' triangular plane structure is similar to that reported for $Na_2[Cu(CN)_3]\cdot 3H_2O$ [16]. The Cu–C atomic distances (1.87–1.96 Å) and the C–N distances (1.13–1.20 Å) are within the range of the corresponding values reported for cyanocuprate(I) complexes [16–20]. Water molecules are not coordinated to copper, and form hydrogen bonds with CN nitrogen atoms.

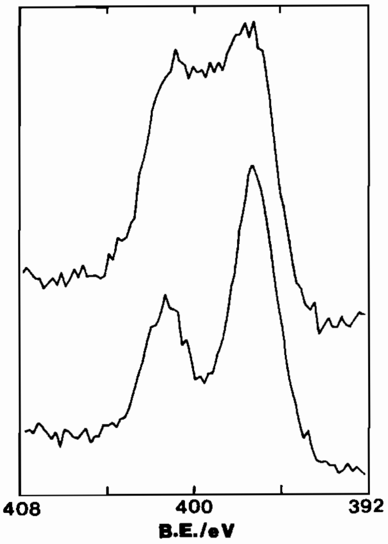


Fig. 2. Nitrogen 1s X-ray photoelectron spectra of $HV^{2+}[Cu^{I}(CN)_3]^{2-}\cdot 2H_2O$ (top) and $MV^{2+}[Cu^{I}_3(CN)_5]^{2-}$ (bottom).

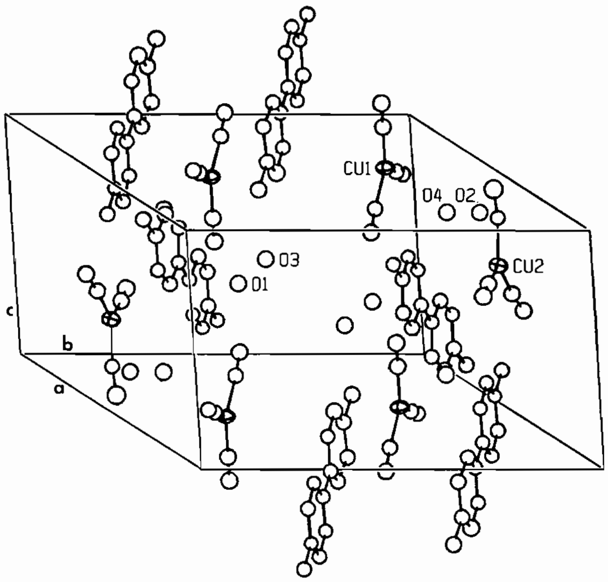


Fig. 3. ORTEP packing diagram for $HV[Cu(CN)_3]\cdot 2H_2O$.

A $[Cu(CN)_3]^{2-}$ anion is stacked face-to-face with an HV^{2+} cation, and a cation–anion pair is formed. There are two crystallographically non-equivalent ion-pairs, I and II, which are shown in Fig. 4. In each pair, a copper atom has a close contact with a carbon atom of a pyridine ring: the Cu–C distance is 3.2 Å. The dihedral angle between a $[Cu(CN)_3]^{2-}$ plane and its neighboring pyridine ring is 7° in pair I and 4° in pair II. Two pyridine rings in each bipyridine cation are almost coplanar with each other: a twist angle is 1° in pair I and 4° in pair II. One of the pyridine rings in a bipyridine cation is close to copper so that the two pyridine rings are no longer equivalent to each other. Three CN ligands in a $[Cu(CN)_3]^{2-}$ are not equivalent due to ion-pair formation (Fig. 4). This was supported by the IR spectrum, in which three CN stretching bands were observed at 2110, 2095 and 2090 cm^{-1}. The heptyl groups were disordered. The location of the most probable positions showed that both heptyl groups of an HV molecule bent away from the ion-pairing side. The steric effects of the heptyl groups prevent the formation of a cation–anion alternating columnar structure. In some methylviologen complexes with metal chelate anions, the formation of a cation–anion contact has been reported with an interplanar distance of 3.2–3.6 Å [11, 14]. When compared with these values, the short interplanar distance of 3.2 Å between HV^{2+} and $[Cu(CN)_3]^{2-}$ suggests that the ion-pair is very stable.

The electronic absorption spectrum observed in a KBr pellet of the powdered material exhibited broad

TABLE 1. Positional parameters and their e.s.d.s of $HV[Cu(CN)_3] \cdot 2H_2O$

Atom	*x*	*y*	*z*	*B* (Å^2)
Cu1	0.2275(3)	0.4000(2)	0.8490(5)	6.2(1)
Cu2	−0.2833(3)	0.8907(2)	0.7169(5)	6.1(1)
O1	0.094(1)	0.509(1)	0.342(2)	6.4(6)*
O2	0.599(1)	0.012(1)	0.214(2)	6.3(6)*
O3	0.010(1)	0.618(1)	0.401(2)	6.9(6)*
O4	0.522(1)	0.127(1)	0.176(2)	6.9(6)*
N61	0.145(1)	0.480(1)	1.078(3)	6.6(7)*
N62	0.353(1)	0.304(1)	0.936(3)	5.8(7)*
N63	0.164(2)	0.426(1)	0.550(3)	7.0(8)*
N64	−0.355(2)	0.976(1)	0.495(3)	6.7(7)*
N65	−0.160(2)	0.796(1)	0.648(3)	7.5(8)*
N66	−0.349(2)	0.918(2)	1.004(3)	8.6(9)*
N1	−0.176(1)	0.815(1)	1.224(2)	4.1(6)*
N2	0.057(1)	0.616(1)	0.830(3)	5.8(7)*
N3	0.338(1)	0.326(1)	1.366(2)	5.1(7)*
N4	0.556(1)	0.116(1)	1.762(3)	5.6(7)*
C61	0.180(2)	0.451(2)	0.996(3)	5.6(9)*
C62	0.307(2)	0.339(2)	0.904(3)	5.6(9)*
C63	0.190(2)	0.415(2)	0.660(3)	6.5(9)*
C64	−0.330(2)	0.940(2)	0.577(3)	6.1(9)*
C65	−0.208(2)	0.831(2)	0.676(3)	6.3(9)*
C66	−0.317(2)	0.910(2)	0.901(3)	4.8(8)*
C1	−0.177(2)	0.818(2)	1.077(3)	5.2(8)*
C2	−0.132(2)	0.780(1)	0.993(3)	4.5(8)*
C3	−0.085(2)	0.739(1)	1.072(3)	4.7(8)*
C4	−0.081(2)	0.737(1)	1.217(3)	4.6(8)*
C5	−0.126(2)	0.775(1)	1.302(3)	4.8(8)*
C6	0.008(2)	0.658(2)	0.760(3)	7(1)*
C7	−0.037(2)	0.698(2)	0.844(3)	4.9(8)*
C8	−0.038(2)	0.696(2)	0.990(3)	5.0(8)*
C9	0.016(2)	0.657(2)	1.058(3)	5.2(8)*
C10	0.058(2)	0.611(2)	0.978(3)	5.6(9)*
C11	0.336(2)	0.331(2)	1.506(3)	5.3(8)*
C12	0.381(2)	0.292(2)	1.591(3)	5.6(9)*
C13	0.426(2)	0.246(2)	1.516(3)	4.8(8)*
C14	0.431(2)	0.247(1)	1.374(3)	4.4(8)*
C15	0.388(2)	0.288(1)	1.298(3)	4.2(8)*
C16	0.514(2)	0.159(2)	1.832(3)	6.1(9)*
C17	0.474(2)	0.207(2)	1.757(3)	5.1(8)*
C18	0.474(2)	0.202(1)	1.611(3)	4.5(8)*
C19	0.522(2)	0.157(2)	1.545(3)	5.2(8)*
C20	0.561(2)	0.112(1)	1.621(3)	4.7(8)*
C21	−0.227(2)	0.859(2)	1.307(3)	5.2(8)*
C22	−0.164(2)	0.934(2)	1.395(4)	11(1)*
C31	0.103(2)	0.570(2)	0.737(3)	6.4(9)*
C32	0.173(2)	0.617(2)	0.721(4)	9(1)*
C41	0.285(2)	0.370(1)	1.280(3)	4.6(8)*
C42	0.345(2)	0.442(2)	1.270(4)	9(1)*
C51	0.602(2)	0.067(2)	1.853(3)	5.7(9)*
C52	0.682(2)	0.113(2)	1.954(4)	8(1)*

For the numbering of the atoms, see Fig. 4. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

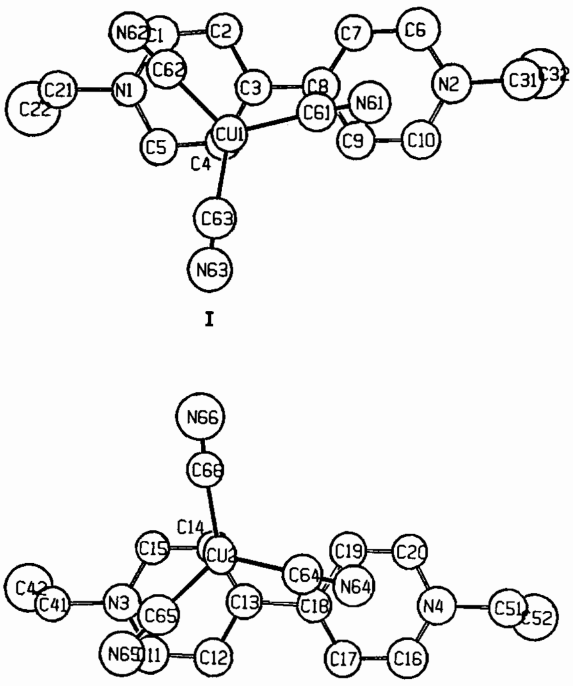
TABLE 2. Bond distances (Å) for $HV[Cu(CN)_3] \cdot 2H_2O$

Cu1–C61	1.94(3)	N4–C16	1.35(4)
Cu1–C62	1.96(3)	N4–C20	1.35(4)
Cu1–C63	1.87(3)	N4–C51	1.57(4)
Cu2–C64	1.88(3)	C1–C2	1.40(4)
Cu2–C65	1.89(3)	C2–C3	1.41(4)
Cu2–C66	1.92(3)	C3–C4	1.37(4)
N61–C61	1.17(4)	C3–C8	1.45(4)
N62–C62	1.14(4)	C4–C5	1.40(4)
N63–C63	1.13(4)	C6–C7	1.40(5)
N64–C64	1.18(4)	C7–C8	1.38(4)
N65–C65	1.17(4)	C8–C9	1.41(4)
N66–C66	1.20(4)	C9–C10	1.42(4)
N1–C1	1.39(4)	C11–C12	1.39(4)
N1–C5	1.41(4)	C12–C13	1.42(4)
N1–C21	1.53(4)	C13–C14	1.37(4)
N2–C6	1.40(4)	C13–C18	1.54(4)
N2–C10	1.41(4)	C14–C15	1.34(4)
N2–C31	1.54(4)	C16–C17	1.43(5)
N3–C11	1.32(4)	C17–C18	1.37(4)
N3–C15	1.38(4)	C18–C19	1.44(4)
N3–C41	1.53(4)	C19–C20	1.36(4)

TABLE 3. Bond angles (°) for $HV[Cu(CN)_3] \cdot 2H_2O$

C61–Cu1–C62	120(1)	C4–C3–C8	120(3)
C61–Cu1–C63	114(1)	C3–C4–C5	123(3)
C62–Cu1–C63	126(1)	N1–C5–C4	113(2)
C64–Cu2–C65	122(1)	N2–C6–C7	118(3)
C64–Cu2–C66	113(1)	C6–C7–C8	125(3)
C65–Cu2–C66	125(1)	C3–C8–C7	123(3)
C1–N1–C5	123(2)	C3–C8–C9	121(3)
C1–N1–C21	119(2)	C7–C8–C9	116(3)
C5–N1–C21	117(2)	C8–C9–C10	122(3)
C6–N2–C10	120(3)	N2–C10–C9	119(3)
C6–N2–C31	118(2)	N3–C11–C12	120(3)
C10–N2–C31	122(2)	C11–C12–C13	116(3)
C11–N3–C15	123(3)	C12–C13–C14	122(3)
C11–N3–C41	117(2)	C12–C13–C18	115(3)
C15–N3–C41	120(2)	C14–C13–C18	123(3)
C16–N4–C20	125(3)	C13–C14–C15	120(3)
C16–N4–C51	117(2)	N3–C15–C14	119(3)
C20–N4–C51	118(2)	N4–C16–C17	120(3)
Cu1–C61–N61	174(2)	C16–C17–C18	117(3)
Cu1–C62–N62	179(2)	C13–C18–C17	122(3)
Cu1–C63–N63	176(3)	C13–C18–C19	119(2)
Cu2–C64–N64	174(2)	C17–C18–C19	120(3)
Cu2–C65–N65	177(3)	C18–C19–C20	121(3)
Cu2–C66–N66	170(2)	N4–C20–C19	117(3)
N1–C1–C2	123(3)	N1–C21–C22	106(2)
C1–C2–C3	113(3)	N2–C31–C32	107(3)
C2–C3–C4	124(3)	N3–C41–C42	105(2)
C2–C3–C8	116(3)	N4–C51–C52	110(2)

humps at *c.* 370 and 500 nm, in addition to a strong 262 nm band. The crystal spectrum was obtained for thin plate-like crystals that were placed on a quartz plate with a drop of water. The spectrum was essentially identical with that obtained in the KBr pellet. The 262 nm band is assigned to an electronic transition within an HV^{2+} cation. The other bands are attributable to an interion charge transfer in an HV^{2+}–$[Cu(CN)_3]^{2-}$ pair, because both HV^{2+} and $[Cu(CN)_3]^{2-}$ ions have closed-shell electronic structures and exhibit no ab-



I

II

Fig. 4. HV^{2+}–$[Cu(CN)_3]^{2-}$ ion pairs, I and II, projected perpendicularly to the anion molecular plane: the closest interion Cu–C distances are 3.21(3) and 3.24(2) Å in pairs I and II, respectively. For heptyl groups, the atomic positions are shown only for the nearest and next-nearest neighboring carbon atoms of nitrogen.

sorption band in the visible region. An aqueous solution of the compound also showed a broad hump at *c.* 350 nm in addition to the 260 nm band. This suggests that the cation–anion pair is formed even in water.

Methylviologen (MV^{2+}) salt

When a methylviologen(2+) chloride solution was mixed with a solution containing NaCN and CuCN in the ratio, NaCN/CuCN = 1, $MV[Cu_3(CN)_5]$ precipitated immediately as a light brown fine powder. For NaCN/CuCN = 2 and 3, a light brown solution was obtained, and after a week, $MV[Cu_3(CN)_5]$ was precipitated as a powder.

The XPS spectrum of copper closely resembled that of $HV[Cu(CN)_3]\cdot 2H_2O$:a $2p_{3/2}$ core-electron peak appeared at a binding energy of 932.3 eV with an FWHM of 2.8 eV and a $2p_{1/2}$ peak at 952.3 eV with an FWHM of 3.4 eV. The shake-up satellites were not observed. The copper atoms, therefore, are in the Cu^I state. The nitrogen 1s spectrum showed two peaks at 397.3 and 401.3 eV with an intensity ratio of 5:2, as shown in Fig. 2. The lower binding energy peak was assignable to a negatively charged nitrogen in CN^- and the higher binding energy peak to a positively charged nitrogen in MV^{2+}. These XPS results are consistent with the composition deduced from the elemental analyses, and showed that the compound could be formulated as $MV^{2+}[Cu^I_3(CN)_5]^{2-}$. As expected for a compound with this stoichiometry, an electron paramagnetic resonance signal was not observed; the compound did not contain paramagnetic species such as Cu^{II} ions and $MV^{+\bullet}$ radicals.

In the IR spectrum, five CN stretching bands were observed at 2130, 2115, 2100, 2090 and 2080 cm^{-1}. There are a number of non-equivalent CN ligands, some of which are probably involved as bridging bidentate ligands as predicted from the compound composition.

The electronic absorption spectrum of the MV complex in a KBr pellet exhibited charge-transfer bands which were essentially identical with those of the HV complex. An aqueous solution showed a broad hump attributable to a charge-transfer transition of *c.* 380 nm. This charge-transfer band was clearly observed for a solution of reaction mixture. These spectroscopic properties suggest that the MV complex contains stable cation–anion pairs resembling those found for the HV complex.

Discussion

Our study has shown that a charge-transfer complex is formed between an electron-accepting viologen cation and an electron-donating cyanocuprate(I) anion; a redox reaction does not occur between these ions. One of the important features of the compound is that a cation–anion pair is formed by a close Cu–C contact. This contact is responsible for the charge-transfer electronic absorption band. Another important feature is that the ion pair is stable even in water. This stability suggests that a color device may be constructed by dissolving this type of charge-transfer complex in an appropriate matrix. Since the electron-donating capacity of copper can be readily controlled by replacing coordinated ligands, the use of a copper complex as the counter anion may provide a variety of charge-transfer viologen complexes applicable to materials used in electronic devices.

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