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Coordination abilities of polycyano anions in the solid state: coordination geometries and d–d transition energies of mixed-ligand solvatochromic copper(II) complexes with $B(CN)_4$, $C(CN)_3$, and $N(CN)_2$ anions

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$B(CN)_4^-$, $C(CN)_3^-$, and $N(CN)_2^-$ are highly versatile polycyano anions that produce various functional compounds. To investigate the coordination abilities of these anions in the solid state quantitatively, we synthesized mixed-ligand Cu(II) complexes: [Cu(R-acac)(tmen)X] (X = polycyano anion, R-acac = acetylacetonate or butyl-acetylacetonate, tmen = tetramethylethylenediamine). The coordination abilities of the anions, increasing in the order $B(CN)_4^- < C(CN)_3^- < N(CN)_2^-$, result in the decrease in the d–d transition energies of the complexes and the shortening of the axial coordination distance. The influence of crystal packing on the coordination geometries and d–d transition energies of the complexes was also demonstrated. The donor numbers of the anions were determined from the d-d transition energies in solution.

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Introduction

The polycyano anions tetracyanoborate ($B(CN)_4^-$), tricyanomethanide ($C(CN)_3^-$), and dicyanamide ($N(CN)_2^-$) are important owing to their versatility in application to various fields of materials science. They have been used as components of metal complexes,[1,2] charge transfer salts,[3] and ionic liquids.[4] These anions produce various coordination polymers because of their multidentate coordination ability.[1] Furthermore, they have recently been used as the precursors of carbon-based materials based on their thermal reactivity. Although the coordination chemistry of $N(CN)_2^-$ anion has been well studied, the examples of transition metal complexes with $C(CN)_3^-$ and, especially, $B(CN)_4^-$ anions are very limited.[1b,c] Moreover, no direct quantitative comparison of these anions has yet been available, except for an NMR study on the coordination abilities of ionic liquids with the polycyano anions.[6] Quantitative evaluation of their coordination strength in the solid state would provide useful information for the design of materials based on these anions.

This study aims at evaluating the coordination ability of the polycyano anions in the solid state by using the solvatochromic mixed-ligand Cu(II) complex $[Cu(acac)(tmen)]^+$ (acac = acetylacetonate, tmen = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) and its derivative.[7] It is known that the coordination of solvent molecules or anions to the metal center changes the color or d–d transition energy of the solvatochromic cationic complex, depending on their coordination ability.[8] The case of anion coordination is shown in Fig. 1a. The solvatochromic property is used to evaluate the donor number (DN), which is a measure of the Lewis basicity, for a number of solvent molecules[8,9] and anions[10] in solutions. As a related study, the correlation between the d–d transition energies and coordination geometries of solvent-coordinated solvatochromic complexes $[Cu(acac)(N\text{^}N)(solvent)]BPh_4$ (N^N = 1,10-phenanthroline, 2,2′-bipyridyl) in the solid state has been investigated.[11]

This paper reports the structures and properties of metal complexes formed from the solvatochromic cations and polycyano anions (Fig. 1b): [Cu(Bu-acac)(tmen)X] (**1-X**) and [Cu(acac)(tmen)X] (**2-X**), where X = $B(CN)_4^-$, $C(CN)_3^-$, and $N(CN)_2^-$ (Bu-acac = 3-*n*-butyl-2,4-pentanedionate). We aim to reveal the correlation between the coordination geometry and coordination ability of the anion and to investigate whether the coordination geometry is affected by the crystal packing. There has been only few crystallographic investigation on anion-coordinated Cu(II) solvatochromic complexes.[12] Another topic of interest was to determine whether these anions can act as multidentate ligands toward solvatochromic complexes. Since we previously found that salts of solvatochromic cations and the bis(trifluoromethanesulfonyl)amide anion ([Cu(acac)(alkyldiamine)]Tf_2N) are ionic liquids,[13] we also became interested in their melting points.

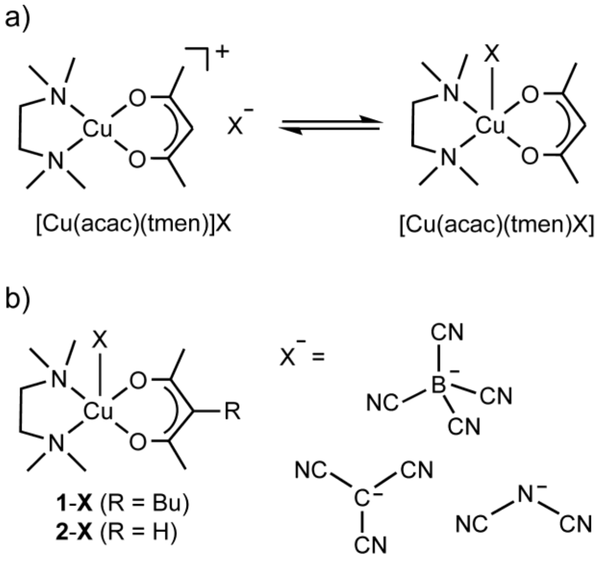

Fig. 1 (a) Coordination equilibrium of the diamine-diketone Cu(II) solvatochromic complex with a coordinating anion. (b) Structural formulae of the complexes synthesized in this study.

Results and Discussion

Preparation and properties

Complexes **1-X** and **2-X** (X = $B(CN)_4^-$, $C(CN)_3^-$, and $N(CN)_2^-$) were synthesized by the reactions of copper(II) nitrate or perchlorate with diamine and diketonate ligands in ethanol, followed by anion exchange. Single crystals of **1-B(CN)$_4$**, **1-C(CN)$_3$**, **2-C(CN)$_3$**, and **2-N(CN)$_2$** were obtained by recrystallization, whereas **1-N(CN)$_2$** and **2-B(CN)$_4$** produced powders containing a small amount of transparent by-product that was difficult to isolate. The color of the crystals depended on the anion: the $N(CN)_2$, $C(CN)_3$, and $B(CN)_4$ complexes were greenish-blue, dark blue, and violet solids, respectively. The color difference reflects the strength of the anion coordination, as shown in the next section. The formation of coordination bonds affected the CN stretching modes in the IR spectra, as seen from the spectral shifts of the complexes compared with those of alkali metal salts (**Table 1**). In particular, the CN stretching mode was observed in the spectra of **1-B(CN)$_4$** and **2-B(CN)$_4$,** whereas it is very weak in the spectrum of $KB(CN)_4$ because of the tetrahedral symmetry of the anion.[14] This result is consistent with the monodentate coordination of the anion to the metal center, which reduces the anion symmetry. Upon heating, **1-B(CN)$_4$** decomposed at 144°C without melting, whereas **1-C(CN)$_3$** melted at 99°C immediately followed by decomposition. This is in striking contrast to [Cu(acac)(alkyldiamine)]Tf_2N, which is an ionic liquid.[13] The weakly coordinating Tf_2N anion effectively produces salts with low melting points, whereas the polycyano anions coordinated to the metal center to produced solids with high melting points.

Table 1 CN stretching frequencies (cm^{-1}) in the IR spectra of the complexes and alkal metal salts.

1-B(CN)$_4$	2223	$KB(CN)_4$	–^{a}
2-B(CN)$_4$	2220		
1-C(CN)$_3$	2157	$KC(CN)_3$	2171
2-C(CN)$_3$	2167		
1-N(CN)$_2$	2249	$NaN(CN)_2$	2285
	2205		2227
	2140		2179
2-N(CN)$_2$	2247		
	2200		
	2138		

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[a]Symmetry forbidden

d–d transition energies

A broad band attributed to d–d transition of the copper(II) ion in the solvatochromic complexes was observed in the visible region. The d–d transition energies of **1-(CN)$_4$**, **1-C(CN)$_3$**, **2-C(CN)$_3$**, and **2-N(CN)$_2$** in dichloroethane (DCE) solutions were determined from the Vis-NIR spectra. The absorption maxima are summarized in Table 2. **1-N(CN)$_2$** and **2-B(CN)$_4$** were not used because of insufficient purity. The d–d transition energies decreased in the order of the salts with $B(CN)_4^- > C(CN)_3^- > N(CN)_2^-$, indicating that the coordination ability of the anion increases in this order.[8] This tendency is reasonable considering that the charge distribution on each cyano group decreases with decreasing number of cyano groups.[6] The DNs of $B(CN)_4^-$, $C(CN)_3^-$, and $N(CN)_2^-$ were determined to be 15.6, 21.1, and 27.5, respectively, based on the relationship $DN = 129.6 - 0.548\ AN_{DCE} - 0.00602\ \nu_{max}$(**2-X** in DCE), where $AN_{DCE} = 16.7$ (AN = acceptor number).[10a] DN of $B(CN)_4^-$ was determined from the spectrum of a mixture of $[NBu_4][B(CN)_4]$ and **2-BPh$_4$** in DCE.[10a] Therefore, the basicity of these and related anions increases in the order: *B(CN)*$_4^-$ (15.6) < $CF_3SO_3^-$ (16.9) < *C(CN)*$_3^-$ (21.1) < CN^- (27.1) < *N(CN)*$_2^-$ (27.5) < NCO^- (40.4), where the DN values[10a] are shown in parenthesis. The DNs of $B(CN)_4^-$, $C(CN)_3^-$, and $N(CN)_2^-$ in the ionic liquid state measured by using ^{23}Na NMR spectroscopy are 20.3, 26.1, and 37.8, respectively,[6] which are larger than the present values. The d–d transition energies of these complexes in the solid state were determined from the solid-state Vis-NIR spectra (Fig. 2), and were found to be red-shifted by 360–570 cm^{-1} relative to those of the complexes in dichloroethane solution, probably due to the effect of crystal packing. A similar red shift in the solid state has been observed in the solvent-coordinated complexes [Cu(acac)(N^N)(solvent)]BPh$_4$.[11] The d–d transition energies of **1-X** were red-shifted relative to those of **2-X** by 740 cm^{-1} (X = B(CN)$_4$), 600 cm^{-1} (X =

$C(CN)_3$), and 30 cm^{-1} (X = $N(CN)_2$). This feature was mainly due to the electron donating nature of the butyl group of the acac ligand in **1-X**, which reduces the Lewis acidity of the metal center to weaken the coordination bond with the axial ligand. This was also supported by the red shift of 600 cm^{-1} in the case of **1-C(CN)₃** relative to that for **2-C(CN)₃**. This tendency was also confirmed crystallographically, as shown in the next section.

Table 2 d–d transition energies of the complexes in dichloroethane solution (5 mM) and in the solid state.

Compound	ν_{max}, in DCE (cm^{-1})	ν_{max}, solid (cm^{-1})
1-B(CN)₄	17953	18315
2-B(CN)₄	17423[a]	17575
1-C(CN)₃	16978	17513
2-C(CN)₃	16502	16920
1-N(CN)₂	–[b]	15974
2-N(CN)₂	15432	16000

[a] Value observed in the solution of **2-BPh₄** and $[NBu_4][B(CN)_4]$ in DCE. [b] Not measured due to impurity.

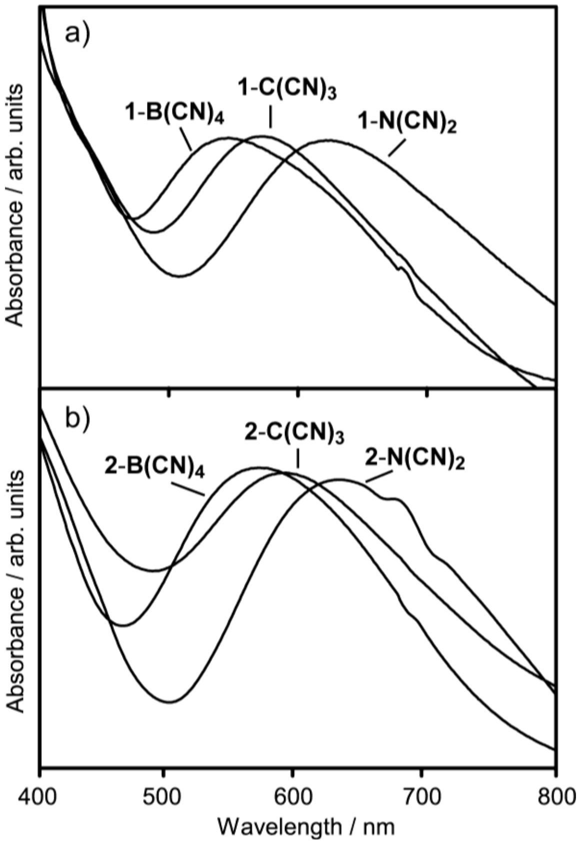

Fig. 2 Vis-NIR spectra of (a) **1-B(CN)$_4$**, **1-C(CN)$_3$**, and **1-N(CN)$_2$** and (b) **2-B(CN)$_4$**, **2-C(CN)$_3$**, and **2-N(CN)$_2$** in the solid state (KBr plates).

Crystal structures

The molecular structures of **1-B(CN)$_4$**, **1-C(CN)$_3$**, **2-C(CN)$_3$**, and **2-N(CN)$_2$** were determined by X-ray crystallography at 100 K. These complexes crystallized in monoclinic space groups $P2_1/n$, $P2_1$, $C2/c$, and $P2_1/n$, respectively. The molecular structures of the complexes are shown in Fig. 3. There were two crystallographically independent molecules in **1-C(CN)$_3$** and **2-N(CN)$_2$**, with slightly different structures. In **1-C(CN)$_3$**, molecule I had a two-fold disorder in the diamine ligand with an occupancy ratio of 0.56:0.44 (Fig. 3b).

The packing diagrams of the complexes are shown in Fig. 4. **1-B(CN)$_4$** adopts a dimer-like molecular arrangement in the crystal, with an intradimer Cu···Cu distance of 5.03 Å (Fig. 4a, dotted line). This arrangement is similar to those in the solvent-coordinated complexes [Cu(acac)(N^N)(solvent)]BPh_4.[11] Notably, the $C(CN)_3$ anion in **1-C(CN)$_3$** is coordinated to the cation plane in a canted orientation (∠Cu–N≡C = 139.0° and 142.4°, Fig. 3b), whereas that in **2-C(CN)$_3$** is oriented nearly perpendicular to the cation plane (∠Cu–N≡C = 175.5°, Fig. 3c), resulting in a dimer-like intermolecular arrangement of the anions with a C···C distance of 3.41 Å (Fig. 4c, dotted line). It seems reasonable that the orientation of such a planar anion is affected by the crystal packing.

The polycyano anions often act as multidentate ligands to form network structures.[1] However, they acted only as monodentate ligands in the present crystals. This is probably due to the smaller energy gain for the coordination of the second ligand to the solvatochromic complex.[11] No significant effect of coordination was found in the anion geometry. $B(CN)_4$ and $C(CN)_3$ exhibited no significant distortion due to coordination. The $N(CN)_2$ anions exhibited bent structures with C–N–C angles of 120.0° and 122.6°.

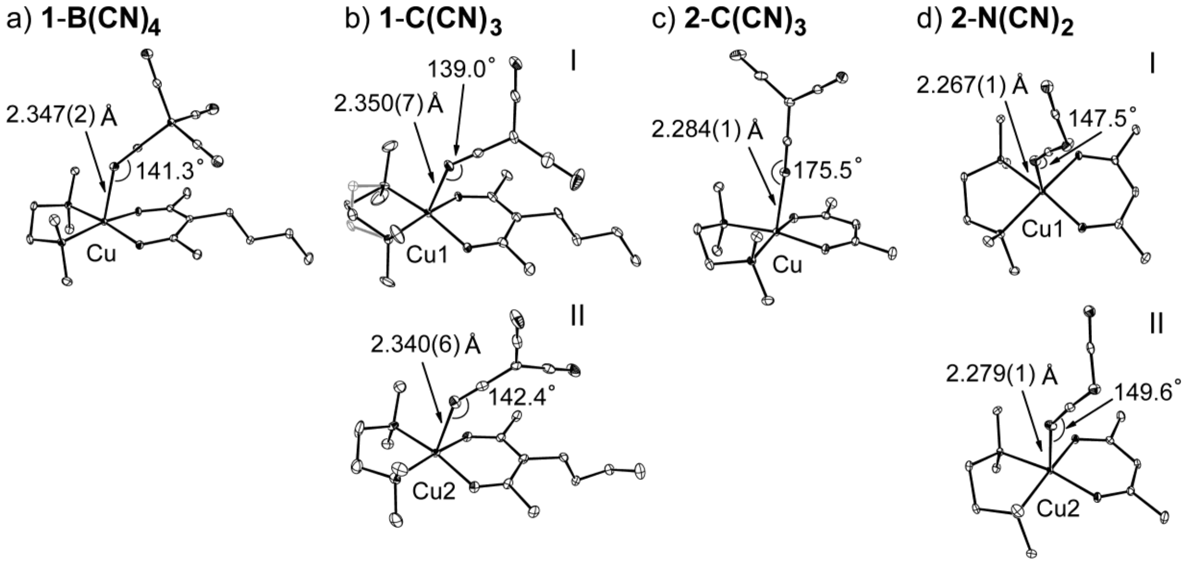

Fig. 3 Molecular structures of (a) **1-B(CN)$_4$**, (b) **1-C(CN)$_3$**, (c) **2-C(CN)$_3$**, and (d) **2-N(CN)$_2$** determined at 100 K. The thermal ellipsoids are drawn at the 30% probability level. Coordination distances (Cu–N) and coordination angles (∠Cu–N≡C) are indicated. Crystallographically independent molecules are designated as I and II. One of the disordered

moieties in molecule I in (b) is displayed in grey. Hydrogen atoms have been omitted for clarity.

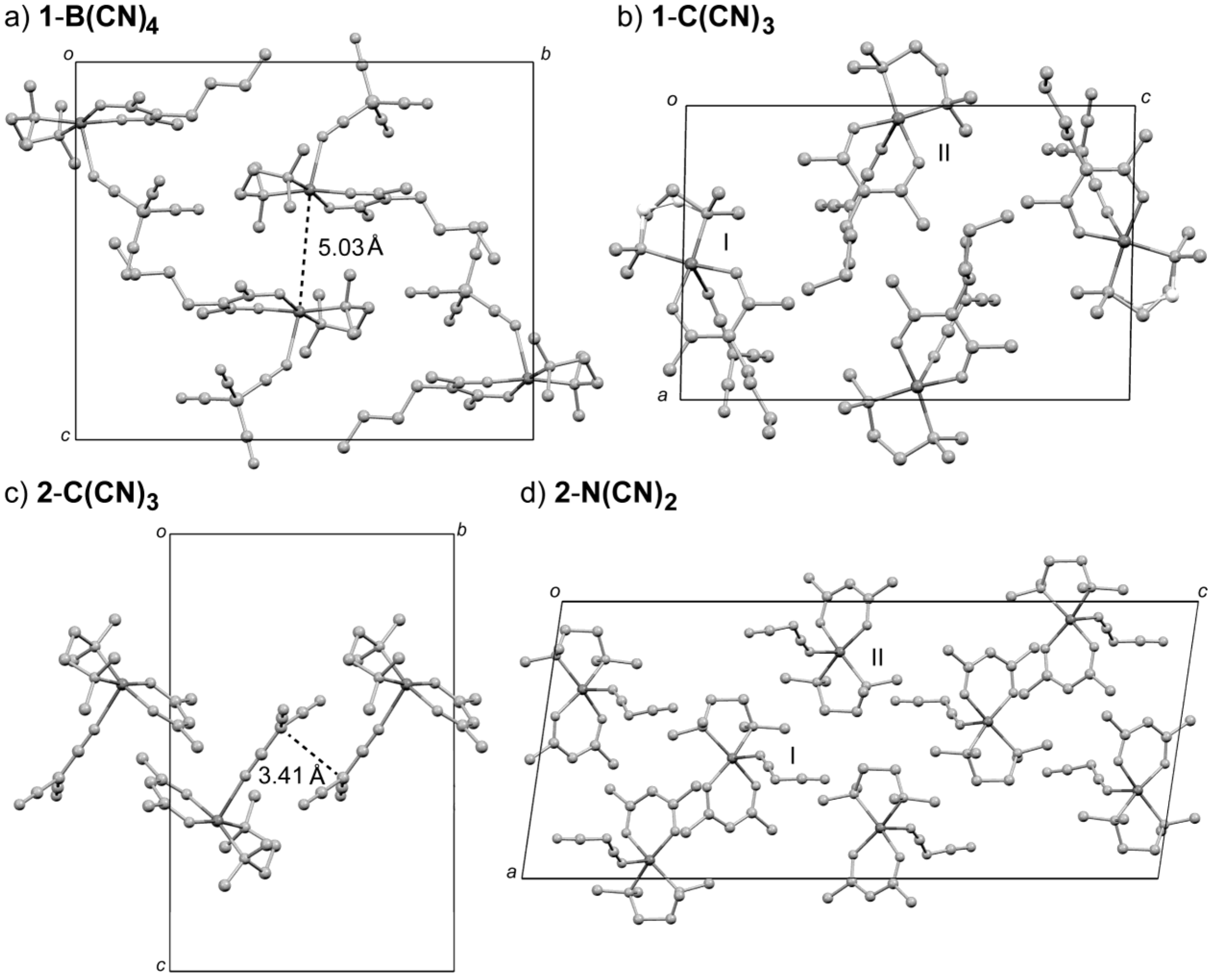
a) 1-$B(CN)_4$ b) 1-$C(CN)_3$ c) 2-$C(CN)_3$ d) 2-$N(CN)_2$

Fig. 4 Packing diagrams of (a) **1-$B(CN)_4$**, (b) **1-$C(CN)_3$**, (c) **2-$C(CN)_3$**, and (d) **2-$N(CN)_2$** at 100 K. Hydrogen atoms have been omitted for clarity. The dotted lines in (a) and (c) represent interatomic distances. One of the disordered moieties in molecule I in (b) is displayed in white.

Anion dependence of coordination geometry

The Cu–N axial coordination distance between the metal center and the anion varied depending on the anion, and decreased in the following order: **1-$B(CN)_4$** (2.347(2) Å) > **1-$C(CN)_3$** (2.350(7), 2.340(6) Å) > **2-$C(CN)_3$** (2.284(1) Å) > **2-$N(CN)_2$** (2.267(1), 2.279(1)

Å). This tendency clearly indicated that the coordination strength increases in the order $B(CN)_4^-$ < $C(CN)_3^-$ < $N(CN)_2^-$, which is consistent with their d–d transition energies. The shorter coordination distance in **2-C(CN)₃** than in **1-C(CN)₃** supported the stronger coordination in **2-X** than in **1-X**, as suggested by their d–d transition energies. In addition, the metal ion was slightly displaced from the basal coordination plane, and the displacement increased with increasing coordination strength in the order **1-B(CN)₄** (0.17 Å) < **1-C(CN)₃** (0.18 Å, average) < **2-C(CN)₃** (0.20 Å) < **2-N(CN)₂** (0.23 Å, average). A similar tendency was also reported for the solvent-coordinated complexes $[Cu(acac)(N^{\wedge}N)(solvent)]BPh_4$.[11]

The correlation between the axial Cu–N coordination distances and d–d absorption energies of the complexes in the solid state is shown in Fig. 5. The trend of increasing d–d transition energy with increasing coordination distance is in accordance with that reported for $[Cu(acac)(N^{\wedge}N)(solvent)]BPh_4$.[11] However, the d–d transition energy in the present complexes is more sensitive to the coordination distance: the energies in the case of **1-X** and **2-X** varied from 16000 cm^{-1} to 18300 cm^{-1} with a the change in the Cu–N distance from 2.27 Å to 2.34 Å, whereas those in the solvent-coordinated complexes varied from 16400 cm^{-1} to 17200 cm^{-1} for the same change in the Cu–O distance.[11] The more pronounced effect of anion coordination may be ascribed to the electrostatic nature of the cation–anion interaction in the complex, though the difference may result partly from the difference of the ligands. The Cu–N coordination distances in these compounds are plotted versus the DN in Fig. 6, together with the Cu–O coordination distances for $[Cu(acac)(N^{\wedge}N)(solvent)]BPh_4$.[11] As seen in this plot, the correlation between DN and coordination distances follows a similar trend for both series. This result demonstrates that the Lewis basicity of solvent molecules and anions is consistently represented in terms of DN.

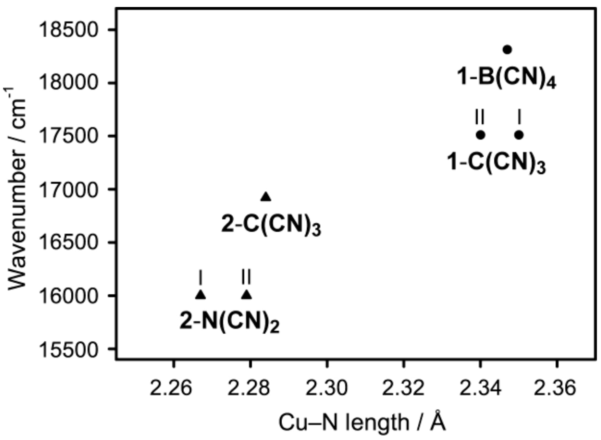

Fig. 5 d–d transition energies (cm^{-1}) of the complexes plotted versus the axial Cu–N bond lengths (Å). Crystallographically independent molecules are indicated by I and II.

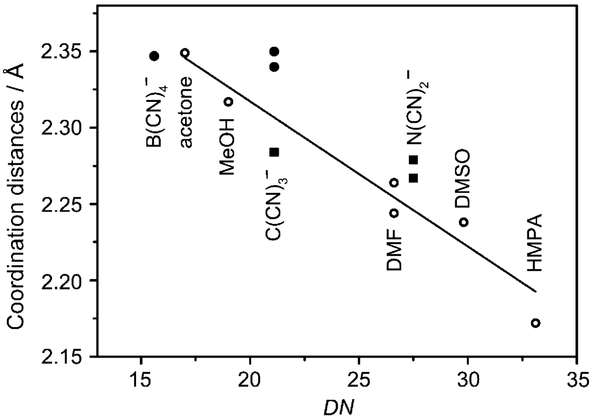

Fig. 6 Coordination distances (Cu–N or Cu–O) in **1-X** (•) and **2-X** (■), and [Cu(acac)(N^N)(solvent)]BPh_4 (N^N = phenanthoroline or bypiridyl: ○) plotted versus DN. Coordinating species are indicated in the figure. The solid line represents the linear correlation for the solvent-coordinated complexes.

Effect of crystal packing on the coordination geometry

Next, we focus on the difference between the coordination geometries of the complexes with the same anion to investigate the effects of crystal packing. There was a significant variation in the axial coordination distances of **1-C(CN)$_3$** and **2-C(CN)$_3$**, while a slight difference was observed in the coordination distances of the two crystallographically independent molecules in **2-N(CN)₂**.

In **1-C(CN)₃**, the Cu–N distances were 2.350(7) Å (molecule I) and 2.340(6) Å (molecule II), which are comparable within the error margin. However, the distance in **2-C(CN)₃** was 2.284(1) Å, shorter than that in **1-C(CN)₃** by 0.06 Å. As seen in the previous section, the orientation of the anion differed in **1-C(CN)₃** and **2-C(CN)₃**, resulting in different coordination angles (∠Cu–N≡C) is 139.0° and 142.4° in **1-C(CN)₃** and 175.5° in **2-C(CN)₃** (Figs. 3b,c). This observation suggested a correlation between the ligand orientation and the coordination distance.

To investigate the aforementioned correlation, DFT calculations were performed on the X-ray geometries of **1-C(CN)₃** (molecule I) and **2-C(CN)₃**. The result for molecule II was essentially the same as that for molecule I. The α-HOMO orbitals of these structures, as shown in Fig. 7, were both composed of the antibonding combination of the HOMO of the anion and a d-orbital of the metal ion. A rather direct σ*-like interaction was found between the orbitals on N and Cu atoms in **1-C(CN)₃** (Fig. 7a), whereas a π*-like interaction was seen in **2-C(CN)₃** (Fig. 7b). This result indicated that the antibonding interaction decreases with increasing coordination angle, which accounts for the shorter coordination distance observed in the latter complex. To verify this tendency, the effect of variation in the coordination angle (∠Cu–N≡C) on the geometry of the optimized structures was investigated. With an increase in the coordination angle from 136.1° (optimized structure without constraints) to 165°, the Cu–N distance decreased almost linearly from 2.153 Å to 2.115 Å. Therefore, it was concluded that variation in the anion orientation due to the packing effect affects the coordination distance.

In **2-N(CN)₂**, the coordination distances in molecules I and II were 2.267(1) Å and 2.279(1) Å, respectively. The difference is 0.01 Å, which is much smaller than that observed in the C(CN)₃ salts. In these molecules, the angles between the anion and cation planes were different (68.7° and 80.3°), whereas the coordination angles were similar (147.5° and 149.6°). Therefore, it is highly probable that the variation in the coordination distances for **2-N(CN)$_2$** also originated from the packing effect, though the difference was small and beyond the accuracy of calculation.

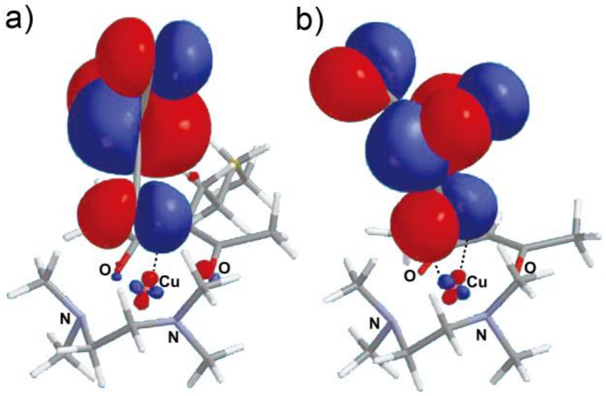

Fig. 7 α-HOMO orbitals of (a) **1-C(CN)$_3$** (molecule I) and (b) **2-C(CN)$_3$** obtained by DFT calculations (B3LYP/Lanl2DZ). The dotted lines indicate interactions between the orbitals on N and Cu.

Conclusions

To evaluate the coordination abilities of polycyano anions, mixed-ligand Cu(II) solvatochromic complexes with anions $B(CN)_4^-$, $C(CN)_3^-$, and $N(CN)_2^-$ were synthesized and crystallographically characterized. The coordination ability of the anions, increasing in the order $B(CN)_4^- < C(CN)_3^- < N(CN)_2^-$, has been quantitatively shown by the decrease in the d–d transition energies and the decrease in the coordination distance between the metal center and the nitrogen atom of the anion. The donor numbers of the anions were determined from their solution spectra. The d–d transition energies in the solid state for the anion-coordinated complexes exhibited a more prominent dependence on the coordination distance than those in the solvent-coordinated complexes [Cu(acac)(N^N)(solvent)]BPh_4. This study also shows that the d–d transition energy and the axial coordination distance are affected by the crystal packing through changes in the anion orientation.

The knowledge obtained through this study on the coordination ability of the polycyano anions would be useful for design and characterization of materials based on these anions. In particular, the weak coordination ability of the $B(CN)_4^-$ anion is noteworthy. Future work will include examination of the coordination abilities of metal-containing functional polycyano anions such as $[M(CN)_n]^-$.

Experimental

General

$[Cu(Bu\text{-}acac)(tmen)]ClO_4$ was synthesized similar to $[Cu(acac)(tmen)]ClO_4$, by using 3-*n*-Butyl-2,4-pentanedione.[7] **2-BPh₄** was synthesized according to the literature.[10a] $[NBu_4][B(CN)_4]$[14] was prepared by metathesis of $K[B(CN)_4]$ and NBu_4Cl, followed by recrystallization from dichloromethane–hexane. Other chemicals were purchased from commercial sources. Potassium tricyanomethanide was recrystallized before use. Melting points were determined using an SRS melting point apparatus MPA100 at a heating rate of 1 K min^{-1}. Elemental analyses were carried out with a PerkinElmer 2400II elemental analyzer. IR spectra were acquired by attenuated total reflectance (ATR) using a Thermo Scientific Nicolet iS5 spectrometer. Vis-NIR spectra were recorded with a JASCO V-570 UV/Vis/NIR spectrometer. DFT calculations (B3LYP/Lanl2DZ) were performed using Spartan ′16.[15]

Preparation of metal complexes

$[Cu(Bu\text{-}acac)\{B(CN)_4\}(tmen)]$ (1-$B(CN)_4$). 3-*n*-Butyl-2,4-pentanedione (0.047 g, 0.30 mmol), sodium carbonate (0.032 g, 0.30 mmol), and *N*, *N*, *N*′, *N*′-tetramethylethylenediamine (0.035 g, 0.30 mmol) were added to a solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.072 g, 0.30 mmol) in ethanol with stirring. After stirring for 30 min, the solution was filtered to remove the unreacted sodium carbonate and the precipitated sodium nitrate. Potassium tetracyanoborate (0.046 g, 0.45 mmol) was added to the filtrate and stirred for a further 30 min. After evaporation, CH_2Cl_2 (10 mL) was added to the residue, and the solution was washed with water (12 mL × 7). The organic layer was dried over magnesium sulfate and the solvent was evaporated. The desired compound was obtained as violet crystals by diffusion of hexane into a CH_2Cl_2 solution of the product (Yield: ~80%). T_m = 144 °C (dec). Elemental analysis calcd (%) for $C_{19}H_{31}O_2N_6BCu$ (449.85 g mol^{-1}): C, 50.73; H, 6.95; N, 18.68; found: C, 50.87; H, 6.71; N, 18.72. IR: $\tilde{\nu}$ = 2223 (CN), 1572, 1455, 1338, 1286, 933, 806 cm^{-1}.

[Cu(Bu-acac){C(CN)$_3$}(tmen)] (1-C(CN)$_3$): This salt was synthesized by the same method described for **1-B(CN)$_4$**, except that potassium tricyanomethanide was used instead of potassium tetracyanoborate. The desired compound was obtained as dark violet crystals (Yield: ~60%). T_m = 99 °C. Elemental analysis calcd (%) for $C_{19}H_{31}O_2N_5Cu$ (425.03 g mol^{-1}): C, 53.69; H, 7.35; N, 16.48; found: C, 53.68; H, 7.14; N, 16.66. IR: $\tilde{\nu}$ = 2157 (CN), 1573, 1450, 1336, 1285, 1018 cm^{-1}.

[Cu(Bu-acac){N(CN)$_2$}(tmen)] (1-N(CN)$_2$): Sodium dicyanamide (0.45 mmol) was added to an aqueous solution of [Cu(Bu-acac)(tmen)]ClO_4 (0.3 mmol), to which CH_2Cl_2 was added and stirred for 30 min. Then, the organic layer was separated and dried with $MgSO_4$, and the solvent evaporated. Then a greenish-blue powder was obtained (Yield: ~50%). However, a small amount of white transparent crystals was formed simultaneously, which could not be fully removed from the product. ESI-MS: *m/z* calcd for [Cu(Bu-acac)(tmen)]$^+$: 334.1682; found: 334.1682. IR: 2249 (CN), 2205 (CN), 2140 (CN), 1579, 1446, 1321, 1011 cm^{-1}.

[Cu(acac){B(CN)$_4$}(tmen)] (2-B(CN)$_4$): This salt was synthesized by the same method described for **1-B(CN)$_4$**, except that acetylacetone was used in place of 3-*n*-butyl-2,4-pentanedione. A violet powder was obtained (Yield: ~50%). However, a small amount of white transparent crystals was formed simultaneously, which could not be fully removed from the product. ESI-MS: *m/z* calcd for [Cu(acac)(tmen)]$^+$: 278.1056; found: 278.1054. IR: $\tilde{\nu}$ = 2220 (CN), 1586, 1518, 1378, 1021, 930 cm^{-1}.

[Cu(acac){C(CN)$_3$}(tmen)] (2-C(CN)$_3$): This salt was synthesized by the same method described for **1-C(CN)$_3$**, except that except that acetylacetone was used instead of 3-*n*-butyl-2,4-pentanedione. The desired compound was obtained as dark blue crystals (Yield: ~50%). Elemental analysis calcd (%) for $C_{15}H_{23}N_5O_2Cu$ (368.93 g mol^{-1}): C, 48.83; H, 6.28; N, 18.98; found: C, 48.61; H, 6.23; N, 19.04. IR: $\tilde{\nu}$ = 2167 (CN), 1580, 1518, 1382, 1021, 779 cm^{-1}.

[Cu(acac){N(CN)$_2$}(tmen)] (2-N(CN)$_2$): This salt was synthesized by the same method described for **2-C(CN)$_3$**, except that sodium dicyanamide were used instead of potassium tricyanomethanide, and extraction was conducted twice. The desired compound was obtained as greenish-blue crystals (yield: ~50%). Elemental analysis calcd (%) for $C_{13}H_{23}O_2N_5Cu$ (344.90 g mol^{-1}): C, 45.27; H, 6.72; N, 20.31; found: C, 45.02; H, 6.48; N, 20.44. IR: $\tilde{\nu}$ = 2247 (CN), 2200 (CN), 2138 (CN), 1519, 1374, 1021, 807 cm^{-1}.

X-ray crystallography

Single crystals of **1-B(CN)$_4$**, **1-C(CN)$_3$**, **2-C(CN)$_3$**, and **2-N(CN)$_2$** were grown by recrystallization from CH_2Cl_2/hexane. X-ray diffraction data were collected on a Bruker APEX II Ultra CCD diffractometer using MoKα radiation (λ = 0.71073 Å). All calculations were performed using SHELXTL. Structures were solved by direct methods (SHELXS 97[16]). The structure of **1-C(CN)$_3$** was refined as a 2-component twin. The non hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed at calculated positions. Ortep-3 for Windows was used to produce molecular graphics.[17] Crystallographic parameters are listed in Table 3. CCDC 1524717 (**1-B(CN)$_4$**), 1524716 (**1-C(CN)$_3$**), 1524715 (**2-C(CN)$_3$**), and 1524714 (**2-N(CN)$_2$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Table 3 Crystallographic parameters.

	1-B(CN)$_4$	**1-C(CN)$_3$**	**2-C(CN)$_3$**	**2-N(CN)$_2$**
empirical formula	$C_{19}H_{31}O_2N_6BCu$	$C_{19}H_{31}CuN_5O_2$	$C_{15}H_{23}CuN_5O_2$	$C_{13}H_{23}CuN_5O_2$
formula weight	449.85	425.03	368.92	344.90
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1$/n	$P2_1$	$C2$/c	$P2_1$/n
a / Å	8.286(8)	10.948(10)	17.6451(19)	13.0071(11)
b / Å	18.723(17)	11.885(11)	11.5250(12)	8.5237(7)
c / Å	15.485(14)	16.734(15)	18.713(2)	29.578(2)
β / deg	94.159(9)	91.091(15)	108.8470(10)	98.2880(10)
V / Å^3	2396.0(4)	2177.0(3)	3601.4(7)	3245.0(5)

Z	4	4	8	8
ρ_{calcd} / g cm^{-3}	1.247	1.297	1.361	1.412
F (000)	948	900	1544	1448
reflections collected	5240	8159	3683	6455
independent reflections	4647	7976	3964	7099
parameters	269	521	214	391
temperature / K	100	100	100	100
$R_1{}^a$, $R_w{}^b$ ($I > 2\sigma$)	0.0349, 0.0922	0.0486, 0.1232	0.0255, 0.0691	0.0246, 0.0696
$R_1{}^a$, $R_w{}^b$ (all data)	0.0395, 0.0954	0.0504, 0.1269	0.0273, 0.0703	0.0273, 0.0710
goodness of fit	1.041	1.091	1.065	1.073

$^aR_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $^bR_w = [\Sigma w (F_o{}^2 - F_c{}^2)^2/\Sigma w (F_o{}^2)^2]^{1/2}$.

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TOC

Crystal structures and electronic spectra of the adducts of polycyano anions with cationic solvatochromic Cu(II) complexes were investigated.