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Structural and spectroscopic comparisons of the square-planar four-coordinate [*o*-phenylenebis(biuretato)]cobaltate(III) complex and the five-coordinate mono- and six-coordinate dicyano adducts

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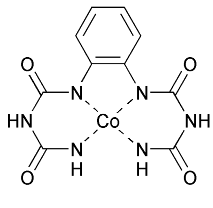
Received 6th July 2001, Accepted 14th November 2001
First published as an Advance Article on the web 7th February 2002

The addition of cyanide ion to the paramagnetic four-coordinate square-planar cobalt(III) complex, $[Co(bbphen)]^-$ {H_4bbphen = *o*-phenylenebis(biuret), $[\mathbf{1}]^-$}, afforded the diamagnetic mono- and dicyano complexes $[Co(bbphen)(CN)]^{2-}$ ($[\mathbf{2}]^{2-}$) and $[Co(bbphen)(CN)_2]^{3-}$ ($[\mathbf{3}]^{3-}$). The X-ray crystal structure analyses of [K(crypt)][**1**] (crypt = cryptand[2,2,2]), $(PPh_4)_2[\mathbf{2}]\cdot 2CH_3CN\cdot H_2O$, and $K_3[\mathbf{3}]\cdot 5.5H_2O$ show them to be a four-coordinate square plane, a five-coordinate square pyramid and a six-coordinate octahedron, respectively. The four-coordinate N atoms of the bbphen ligand in the three complexes were located in a basal plane around the central cobalt atom. The average Co–N bond lengths become longer with increasing coordination number. A novel interactive contact between one of the potassium ions and both the cyano ligand and the phenyl ring of the bbphen ligand is found in $K_3[\mathbf{3}]\cdot 5.5H_2O$. Complex $[\mathbf{2}]^{2-}$ exhibits characteristic intense CT absorption bands at 14.0×10^3 ($\varepsilon = 1380$) and 22.7×10^3 cm^{-1} ($\varepsilon = 1480$ dm^3 mol^{-1} cm^{-1}) together with the distinctively high field ^{13}C NMR chemical shift of the coordinated cyanide ion at 81.5 ppm, as compared with 143.0 ppm for $[\mathbf{3}]^{3-}$ in DMSO.

Introduction

The coordination chemistry of biuret $[H_2NC(O)NHC(O)NH_2]$ complexes has extensively been investigated with various kinds of metal ions since the 1960s because of its variety of coordination mode and the source of the biuret reaction. The most noteworthy property of the biuretate dianion $[HNC(O)NHC(O)NH^{2-}]$ is its strong σ-donor ability which can stabilize unusual high oxidation states, such as Ni^{III}, Cu^{III}, Pd^{III},[1] or four-coordinate Co^{III} complexes. Structural and magnetochemical investigation has demonstrated that some bis(biuretato)cobaltate(III)-type complexes take the four-coordinate square-planar geometry with an intermediate spin ground state ($S = 1$).[2] In spite of their coordinative unsaturation, there have only been a few studies on ligand addition reactions. As reported by Birker *et al.*,[3] the addition reactions of (bbphen)cobaltate(III) anion [bbphen = *o*-phenylenebis(biuretato)], $[\mathbf{1}]^-$ (Scheme 1), with several organic amines or triphenylphosphine in organic solvents gave the diamagnetic Co^{III} products, which was revealed in the magnetic susceptibility and the absorption spectra. They suggested that the products with amines and triphenylphosphine were six- and five-coordinate adduct complexes, respectively. A series of X-ray structures of four-, five- and six-coordinate complexes could be expected to provide some systematic structural information associated with the difference in coordination number. However, no addition reaction product from bis(biuretato)cobaltate(III)-type complexes has been isolated in crystalline form so far, although the corresponding products from other diamagnetic four-coordinate cobalt(III) complexes bearing tetradentate or two bidentate ligands, such as porphyrins[4] or oximes, *etc.*,[5] have been reported.



$[Co(bbphen)]^-$, $[\mathbf{1}]^-$

Scheme 1 The four-coordinate complex, $[Co(bbphen)]^-$.

The present paper deals with the isolation of novel mono- and dicyano complexes. Their spectroscopic properties in both the solid state and solution have been characterised, together with their solution structures. The molecular structures of a series of four-, five- and six-coordinate bbphen complexes have been determined by X-ray crystal structure analysis. This study is the first example of the complete isolation and characterisation of four-, five- and six-coordinate complexes each bearing common basal and monodentate ligands.

Experimental

Syntheses

o-Phenylenebis(biuret) and K[**1**]·DMSO were prepared according to the method described by Birker *et al.*[6]

[K(crypt)][1]. To an aqueous solution (25 cm^3) of K[**1**]·DMSO (0.23 g, 0.50 mmol) was added cryptand[2,2,2] (crypt; 0.19 g, 0.50 mmol) with stirring. The mixture was stirred for 6 h at room temperature to give dark-red cubic crystals of [K(crypt)][**1**] (0.34 g, 90%). The crystals were collected by filtration and washed with water. Mp 203–205 °C (with decomposition). Found: C, 44.80; H, 5.78; N, 14.91%. $C_{28}H_{44}N_8O_{10}$-CoK requires C, 44.80; H, 5.91; N, 14.93%; $\bar{\nu}_{max}/cm^{-1}$ (KBr): 1616vs, 1671s ν(CO). Crystals suitable for X-ray analysis were grown from DMSO solution diluted with water at 40 °C.

PPh_4[1]·H_2O. PPh_4Cl (0.19 g, 0.50 mmol) in water (40 cm^3) was added to K[**1**]·DMSO (0.23 g, 0.50 mmol) in water (50 cm^3). The mixture was stirred at room temperature. The purple precipitate of $PPh_4[\mathbf{1}]\cdot H_2O$ (0.53 g, 79%) which formed was filtered off,

DOI: 10.1039/b106001p

washed with water, and dried *in vacuo*. Mp 211–213 °C. Found: C, 58.84; H, 4.19; N, 12.11%. $C_{34}H_{30}N_6O_5CoP$ requires C, 58.97; H, 4.37; N, 12.13%; $\bar{\nu}_{max}$/cm^{-1} (KBr): 1600vs, 1658s ν(CO).

$(PPh_4)_2$[2]·$2CH_3CN$·H_2O. To a purple chloroform solution (30 cm^3) of PPh_4[**1**]·H_2O (0.069 g, 0.10 mmol) was added KCN (0.065 g, 1.0 mmol). The mixture was stirred for 15 min, giving a green solution. After PPh_4Cl (0.037 g, 0.10 mmol) was added to the solution, the mixture was filtered off to remove the orange precipitate which formed. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in the minimum amount of acetonitrile. The filtrate was allowed to stand at room temperature for a few days. The green prismatic crystals of $(PPh_4)_2$[**2**]·$2CH_3CN$·H_2O deposited were collected by filtration (0.030 g, 27 %), and recrystallized from acetonitrile–diethyl ether. Mp: 193–196 °C. Found: C, 66.08; H, 4.87; N, 11.00%. $C_{63}H_{56}N_5O_5CoP_2$ requires C, 66.37; H, 4.95; N, 11.06%; $\bar{\nu}_{max}$/cm^{-1} (Nujol): 1561s, 1582s ν(CO); 2114 ν(CN).

K_3[3]·$5.5H_2O$. A mixture of K[**1**]·DMSO (0.023 g, 0.050 mmol) and KCN (0.06 g, 1.0 mmol) in water (10 cm^3) was allowed to stand at room temperature for 48 h. The orange precipitate of K_3[**3**]·$3H_2O$ (0.53 g 79%) which formed was collected by filtration and dried *in vacuo*. Mp 250–254 °C (with decomposition). Found: C, 25.73; H, 2.47; N, 19.86%. $H_{14}C_{12}N_8O_7K_3Co$ (= K_3[**3**]·$3H_2O$) requires C, 25.81; H, 2.53; N, 20.06%; $\bar{\nu}_{max}$/cm^{-1} (Nujol): 1553s, 1589s ν(CO); 2109, 2123 ν(CN). Orange prismatic crystals suitable for an X-ray diffraction study were grown from a mixture of water and ethanol.

Measurements

UV-vis absorption spectra were obtained on a Perkin Elmer Lambda 19 spectrophotometer at 23 °C. The solid state absorption spectra in the form of Nujol mulls were obtained according to the method described by Lee *et al.*[7] ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX 270 spectrometer at 30 °C, referenced to tetramethylsilane (TMS) or sodium trimethylsilylpropionic acid-d_4 (TSP-d_4). Samples for ^{13}C NMR chemical shift analysis of coordinated CN^- were prepared by using ^{13}C-enriched KCN (99 atom% ^{13}C). ES mass spectra were recorded on a Perkin Elmer API 300 mass spectrometer. Infrared spectra were obtained on a Perkin Elmer FT IR GX spectrophotometer.

Crystallography

A crystal of each compound, [K(crypt)][**1**], $(PPh_4)_2$[**2**]·$2CH_3CN$·H_2O and K_3[**3**]·$5.5H_2O$, suitable for the X-ray diffraction study was glued on the top of a glass fibre with epoxy resin. The X-ray intensities were measured on Rigaku AFC-5R or -7R instruments [23 °C, λ(Mo-Kα) = 0.71073 Å]. There was no serious decomposition of crystals during data collection. The intensities were corrected for Lorentz-polarization and absorption effects. The structures were solved by the usual heavy-atom method using the SHELXS-86 program,[8] and refined on F^2 by full-matrix least-squares using anisotropic thermal parameters for all non-hydrogen atoms. H atoms of the complex anions and counter cations {[K(crypt)]$^+$ or $PPh_4{}^+$} were introduced at the positions generated by Fourier-difference syntheses or theoretical calculations, and fixed during the structure refinement cycles. The hydrogen atoms of the solvated molecules were not included. All the calculations were carried out using complex neutral atom scattering factors[9] and the TEXSAN software package.[10]

For the crystal of K_3[**3**]·$5.5H_2O$, one of the three K atoms showed positional disorder over two possible positions, K(3a) and K(3b). Assuming an equal population (= 0.5) for each of these two K atoms, a reasonable structure refinement with their anisotropic thermal parameters was obtained. One of the O atoms [O(10)] of the hydrated water molecules was treated as a half occupancy, since the atom was located at a position close (0.87 Å) to the crystallographic inversion center. Crystal data are summarized in Table 1, and selected bond lengths and angles in Table 2.

CCDC reference numbers 169288–169290.

See http://www.rsc.org/suppdata/dt/b1/b106001p/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystallographic studies

In this study, the crystal structures of [K(crypt)][**1**], $(PPh_4)_2$[**2**]·$2CH_3CN$·H_2O and K_3[**3**]·$5.5H_2O$ have been determined by X-ray analysis. The complexes, [**2**]$^{2-}$ and [**3**]$^{3-}$, provide the first example of X-ray crystal structure analyses of a set of ligand addition products from a bis(biuretato)cobaltate(III)-type precursor. The molecular structures of the complex anions, [**1**]$^-$, [**2**]$^{2-}$ and [**3**]$^{3-}$, are shown in Fig. 1, 2 and 3, respectively, together with the atom numbering scheme. Complex [**1**]$^-$ has four-coordinate square-planar (SP-4) geometry, similarly to other bis(biuretato)cobaltate(III)-type complexes.[2] The coordination geometry of [**2**]$^{2-}$ is best described as a five-coordinate square pyramid (SPY-5), comprising an apical C and four basal N donor atoms, although there is a slight distortion toward the trigonal bipyramidal geometry. In fact, the Co atom is displaced by 0.22 Å above the mean plane of the four N donor atoms. The angles N(1)–Co–N(4) (161.8°) and N(4)–Co–C(11) (103°; see Table 2) are smaller and larger, respectively, than the ideal values for the SPY-5 structure. The structure of complex [**3**]$^{3-}$ is close to a six-coordinate octahedron (OC-6) with four basal N and two axial C donors.

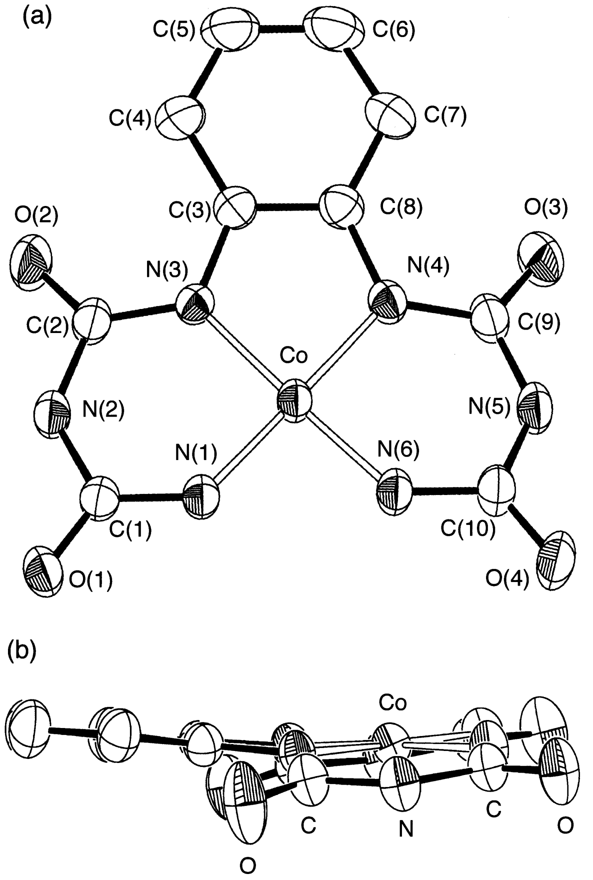


Fig. 1 Top (a) and side (b) views of [Co(bbphen)]$^-$ in [K(crypt)][**1**] with atom-numbering scheme. H atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability level.

Table 1 Crystallographic data for [K(crypt)][**1**], $(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$ and K_3[**3**]$\cdot 5.5H_2O$

Compound	[K(crypt)][**1**]	$(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$	K_3[**3**]$\cdot 5.5H_2O$
Formula	$C_{28}H_{44}KN_8O_{10}Co$	$C_{63}H_{35}N_9O_5P_2Co$	$C_{12}H_{19}K_3N_8O_{9.5}Co$
M	750.73	1134.03	603.56
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	13.540(2)	13.579(3)	11.126(3)
b/Å	16.692(4)	16.696(5)	12.813(2)
c/Å	15.317(3)	13.047(4)	9.737(2)
α/°	90	96.82(3)	112.19(1)
β/°	93.92(1)	101.26(2)	114.59(2)
γ/°	90	101.25(2)	79.37(2)
U/Å^3	3453(1)	2807(1)	1168.2(5)
Z	4	2	2
D_c/Mg m^{-3}	1.444	1.349	1.716
F(000)	1576	1188	614
μ(Mo-Kα)/mm^{-1}	0.683	0.422	1.332
No. of reflns measured	10456	10812	5151
No. of reflns used	10074	10442	4873
No. of parameters	433	721	348
$R1^a$, $wR2^b$	0.042, 0.096	0.069, 0.126	0.065, 0.176

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma_c^2(F_o^2) + (pF_o^2)^2$, p = 0.03 ([K(crypt)][**1**]), 0.02 $(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$ and K_3[**3**]$\cdot 5.5H_2O$.

Table 2 Selected bond lengths (Å) and angles (°) for [**1**]$^-$, [**2**]$^{2-}$ and [**3**]$^{3-}$

	[**1**]$^-$	[**2**]$^{2-}$	[**3**]$^{3-}$
Co–N(1)	1.835(2)	1.878(5)	1.915(4)
Co–N(3)	1.867(2)	1.905(4)	1.918(4)
Co–N(4)	1.867(2)	1.891(4)	1.908(4)
Co–N(6)	1.829(2)	1.874(5)	1.914(4)
Co–C(11)		1.821(7)	1.925(5)
Co–C(12)			1.937(6)
O(1)–C(1)	1.242(3)	1.250(6)	1.270(6)
O(2)–C(2)	1.215(3)	1.229(7)	1.263(6)
O(3)–C(9)	1.225(3)	1.253(7)	1.267(6)
O(4)–C(10)	1.237(3)	1.258(7)	1.284(6)
N(1)–C(1)	1.335(3)	1.321(7)	1.311(6)
N(3)–C(2)	1.376(3)	1.375(7)	1.331(6)
N(3)–C(3)	1.418(3)	1.401(7)	1.419(6)
N(4)–C(8)	1.420(3)	1.396(7)	1.422(6)
N(4)–C(9)	1.386(3)	1.357(7)	1.333(6)
N(6)–C(10)	1.345(3)	1.321(7)	1.288(6)
N(7)–C(11)		1.158(7)	1.157(7)
N(8)–C(12)			1.128(8)
C(3)–C(8)	1.408(3)	1.414(8)	1.417(7)
N(1)–Co–N(3)	92.88(8)	93.1(2)	91.8(2)
N(1)–Co–N(4)	177.43(8)	161.8(2)	176.1(2)
N(1)–Co–N(6)	88.23(8)	87.4(2)	93.5(2)
N(1)–Co–C(11)		95.0(2)	89.3(2)
N(1)–Co–C(12)			88.6(2)
N(3)–Co–N(4)	85.81(8)	85.0(2)	84.3(2)
N(3)–Co–N(6)	178.22(8)	172.2(2)	174.6(2)
N(3)–Co–C(11)		92.7(2)	90.4(2)
N(3)–Co–C(12)			91.6(2)
N(4)–Co–N(6)	93.13(8)	92.0(2)	90.4(2)
N(4)–Co–C(11)		103.1(2)	90.9(2)
N(4)–Co–C(12)			91.4(2)
N(6)–Co–C(11)		95.0(2)	88.5(2)
N(6)–Co–C(12)			89.6(2)
C(11)–Co–C(12)			177.1(2)
Co–N(3)–C(3)	113.3(1)	112.6(3)	111.7(3)
Co–N(4)–C(8)	113.2(1)	112.4(4)	111.6(3)
N(3)–C(3)–C(8)	113.5(2)	113.6(5)	113.8(4)
N(4)–C(8)–C(3)	113.6(2)	115.0(5)	114.0(4)
Co–C(11)–N(7)		176.8(6)	178.0(5)
Co–C(12)–N(8)			175.6(7)

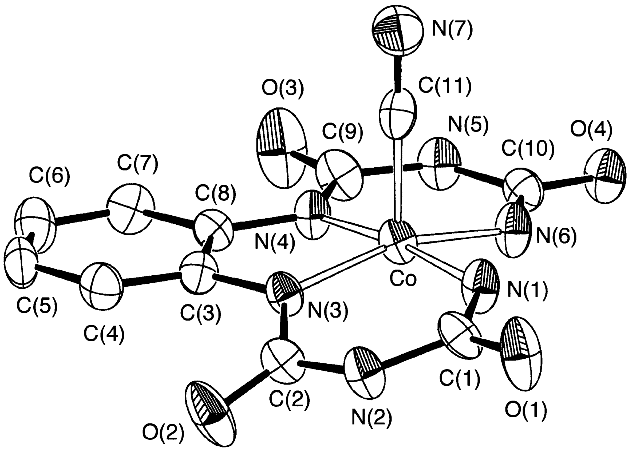


Fig. 2 Perspective drawing of $[Co(bbphen)(CN)]^{2-}$ in $(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$ with atom-numbering scheme. H atoms are omitted for clarity and the thermal ellipsoids are drawn at 50% probability level.

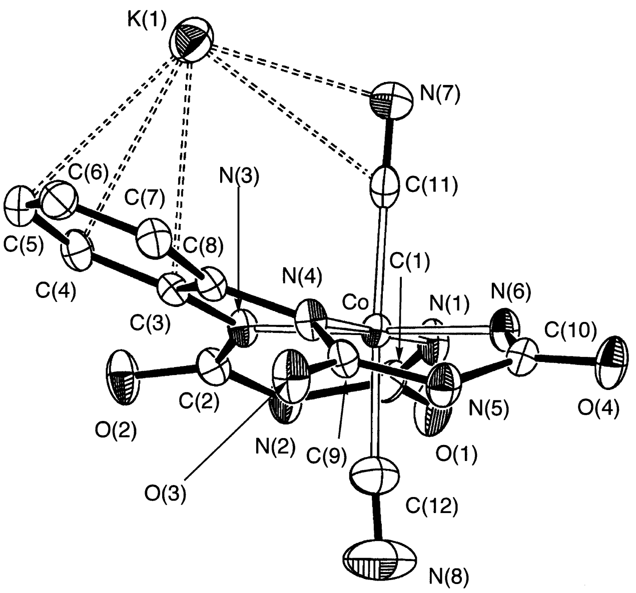


Fig. 3 Perspective drawing of $[Co(bbphen)(CN)_2]^{3-}$ and one of K atoms in K_3[**3**]$\cdot 5.5H_2O$ with atom-numbering scheme. The dotted line indicates multiple interaction between the K^+ and the ligands in [**3**]$^{3-}$. H atoms are omitted for clarity, and the thermal ellipsoids are drawn at 50% probability level.

The average Co–N bond lengths become longer in the order [**1**]$^-$ < [**2**]$^{2-}$ < [**3**]$^{3-}$, the average values being 1.850(2), 1.887(5) and 1.914(6) Å, respectively. The Co–N bond lengths of [**1**]$^-$ or [**3**]$^{3-}$ are in accordance with those of the other Co^{III} complexes having four[2,11] or six[12] deprotonated imino donor groups, respectively. For the increasing Co–N bond lengths in [**1**]$^-$, [**2**]$^{2-}$

and $[\mathbf{3}]^{3-}$, there are two causes to be considered; the total charge and the coordination number among the three complexes. Other types of SPY-5 and OC-6 complexes containing the Co(bbphen) moiety, *e.g.* $[Co(bbphen)(P(OEt)_3)]^-$ and $[Co(bbphen)(piperidine)_2]^-$, have also been prepared and structurally characterized. The average Co–N bond lengths of the bbphen in these cases are found to be 1.877(6) and 1.908(3) Å, respectively.[13] Since they are both uninegative complexes, there is no influence on the bond lengths from the difference in total charge. The bond length variation is solely due to the difference in coordination number. That is, the Co–N bond lengths become longer as the coordination number increases. The above Co–N bond length variation from SP-4 to OC-6 is similar to that for the cyano complexes under consideration here. This fact indicates that the Co–N bond length of the Co(bbphen) moiety is more sensitive to the coordination number than the total charge, as stated by the third bond variation rule.[14] The same trend is seen in bis(oximato)cobalt(III) complexes with pyridine[15] or iodide,[16] although each of these complexes contains a different equatorial tetradentate oximato derivative.

Systematic changes in the bond lengths due to the coordination number of Co^{III} are also observed for the N–C and C=O bonds of the biuretato moiety. The N(coordinated)–C bonds, N(1)–C(1), N(3)–C(2), N(4)–C(9) and N(6)–C(10), become shorter in the order $[\mathbf{1}]^- > [\mathbf{2}]^{2-} > [\mathbf{3}]^{3-}$, while the C=O bonds become longer in the same order. It is suggested that these bond length variations result in a redistribution of the electron density throughout the complex anions, according to the second bond variation rule.[14]

In the crystals of [K(crypt)][**1**] and $(PPh_4)_2[\mathbf{2}]\cdot 2CH_3CN\cdot H_2O$, there is no interaction between the counter cation and the complex anion. In contrast, a significant cation–anion interactive contact exists in the crystal of $K_3[\mathbf{3}]\cdot 5.5H_2O$; one of the K^+, K(1), is close to both the phenyl ring and coordinated CN ligand. The distances between K(1) and three C atoms, [C(3), C(4), C(5)], of the phenyl ring are 3.203(6)–3.335(5) Å.[17] These distances are close to the sum of the ionic radius for K^+ (1.4–1.5 Å) and the half thickness (1.7 Å) of the phenyl ring. They are also within the range found in structural and theoretical studies concerning the interaction between alkali metal cations and some benzyl fragments.[18,19] The distances K(1) ··· C(11) and K(1) ··· N(7) are 3.275(5) and 2.846(6) Å, respectively. Furthermore, the C(11)–N(7) bond of the CN^- concerned is longer than C(12)–N(8) of the other cyano ligand in $K_3[\mathbf{3}]\cdot 5.5H_2O$. These facts may indicate that the η^2 or side-on interaction between K(1) and C(11)–N(7) forces the interacting C–N bond to become weaker, in contrast to the η^1 or end-on interaction between a cyano ligand and a K^+ cation.[20] This could be related to the observation of two IR bands indicating two kinds of cyano ligands with respect to the interaction between the N atom of a CN^- and the K^+ cation, as mentioned before. To the best of our knowledge, this is the first example of a multi-centred interaction between a K^+ ion, a CN^- and a phenyl ring.

Spectroscopic properties

The spectroscopic data for $[\mathbf{1}]^-$, $[\mathbf{2}]^{2-}$ and $[\mathbf{3}]^{3-}$ are tabulated in Table 3 and their absorption spectra are shown in Fig. 4. The absorption spectrum of [K(crypt)][**1**] in $CHCl_3$ or DMSO is similar to that in the solid state, suggesting that the planar four-coordinate SP-4 structure of $[\mathbf{1}]^-$ seen in the crystal structure is maintained in $CHCl_3$ and DMSO.[21] On the other hand, the absorption spectrum of K[**1**]·DMSO in H_2O shows the characteristics of the ligand field d–d transition in OC-6 coordination. Such a solvent dependence of the coordination number is also observed in the ^1H NMR spectrum. [K(crypt)][**1**] in $CDCl_3$ or DMSO-d_6 exhibits a ^1H NMR signal due to phenylene protons with paramagnetic shifts. In contrast, for K[**1**]·DMSO in D_2O, ^1H NMR signals are observed in the diamagnetic region (6.5–9.0 ppm). These signals are broad, probably due to a small amount of the residual paramagnetic species. These facts suggest that [K(crypt)][**1**]·DMSO in $CHCl_3$ or DMSO exists as the SP-4 complex and K[**1**]·DMSO in water forms the aqua complex.

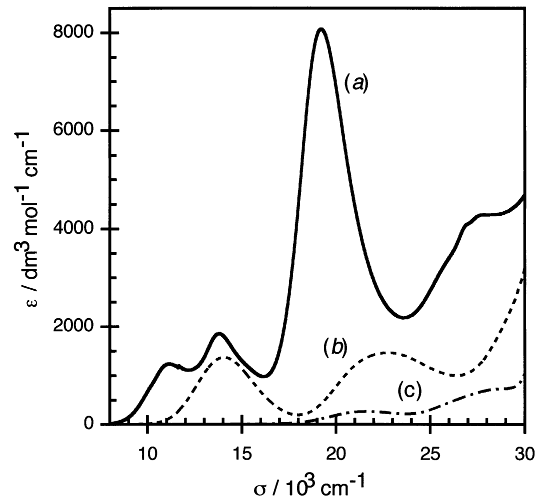


Fig. 4 Absorption spectra of K[**1**]·DMSO in DMSO (a), $(PPh_4)_2[\mathbf{2}]\cdot 2CH_3CN\cdot H_2O$ in DMSO (b) and $K_3[\mathbf{3}]\cdot 5.5H_2O$ in H_2O (c).

In the ES mass spectrum of K[**1**]·DMSO in H_2O, a large amount of $[\mathbf{1}]^-$ was detected, together with a small of amount of $[Co(bbphen)(H_2O)]^-$ and $[Co(bbphen)(H_2O)_2]^-$ (Table 4). This is considered to result from the dissociation of the aqua ligands during the ionization process.

The absorption spectra of $(PPh_4)_2[\mathbf{2}]\cdot 2CH_3CN\cdot H_2O$ in DMSO and $K_3[\mathbf{3}]\cdot 5.5H_2O$ in water are very similar to those for the respective solids. The ES mass spectra of these two complexes indicate the presence of $[\mathbf{2}]^{2-}$ or $[\mathbf{3}]^{3-}$, as shown in Table 4. The ^1H NMR spectra of $(PPh_4)_2[\mathbf{2}]\cdot 2CH_3CN\cdot H_2O$ in DMSO-d_6 and $K_3[\mathbf{3}]\cdot 5.5H_2O$ in D_2O showed phenylene-H signals with the AA′BB′ pattern and without paramagnetic shifts. (Table 3) These facts suggest that the five- and six-coordinate structures of $[\mathbf{2}]^{2-}$ and $[\mathbf{3}]^{3-}$, respectively, are maintained in solution. The ν(CN) band of $(PPh_4)_2[\mathbf{2}]\cdot 2CH_3CN\cdot H_2O$ appears at 2114 cm^{-1}, where the corresponding band has been observed for the other SPY-5 complexes. (Table 5)[22,23] Meanwhile, if the two cyano ligands in $[\mathbf{3}]^{3-}$ have a *trans* dicyano structure, they should be effectively identical and therefore only one ν(CN) band should be observed because only one of two expected vibration modes is infrared active. In the infrared spectrum of $K_3[\mathbf{3}]\cdot 5.5H_2O$, however, two IR bands are observed at 2123 and 2109 cm^{-1}. This observation is in accord with the existence of two kinds of CN bonds (long and short), as found in the X-ray crystal structure analysis (*vide supra*).

The dicyano complex, $K_3[\mathbf{3}]\cdot 5.5H_2O$ in H_2O gives a weak absorption band at 21.8×10^3 cm^{-1} and a shoulder at 28.9×10^3 cm^{-1}. The positions and intensities are typical of the ligand field d–d transition for low-spin OC-6 Co^{III} complexes. The longer wavelength band is located near the first band of the tris(biuretato) complex,[12] for which the ligand field is analogous to the bbphen ligand. The shorter wavelength band is fairly close to the averaged value of the first band of the tris(biuretato) and hexacyano Co^{III} complexes. As predicted by the AOM treatment,[24] two bands at 21.8×10^3 and 28.9×10^3 cm^{-1} can be assigned the tetragonal components $^1A_2$ and $^1E_a \longleftarrow {}^1A_1$ in the first absorption bands, respectively. For the monocyano complex, the first absorption band positions are expected to be located at 19.6×10^3 ($^1E_a \longleftarrow {}^1T_1$) and 21.8×10^3 cm^{-1} ($^1A_2 \longleftarrow {}^1T_1$) from that of the dicyano complex and $[Co(biuretato)_3]^{3-}$ [12] in terms of the holohedrized symmetry assumption of the AOM.[24] This assumption can be substantiated for OC-6-$[NiX_2(Im)_4]$[25] and SPR-5-$[NiX(2\text{-}MeIm)_4]$ ($X = Cl^-$ and Br^-).[26] However, these expected d–d transition bands are hidden by the intense absorption bands which are probably due to CT.

Table 3 Absorption and ^{1}H NMR spectral data

	Absorption data, $\sigma/10^3$ cm^{-1} (log {ε/dm^3 mol^{-1} cm^{-1}})			^{1}H NMR data, δ	
Compound	Solvent	Solution	Solid[a]	Phenyl	Amido[b]
K[**1**]·DMSO	DMSO	11.2 (3.09), 13.8 (3.27), 19.2 (3.91) 23.7 (3.34), 31.4sh (3.76)		−27.5 (s, br), −6.1 (s, br)	−6.4, 2.5
[K(crypt)][**1**]	$CHCl_3$	10.7 (3.10), 13.4 (3.12), 18.8 (3.63) 22.2 (3.14), 31.2sh (3.70)	10.5, 13.5 18.7	−31.9 (s, br), −7.4 (s, br)	−7.7, 3.5
K[**1**]·DMSO	H_2O	15.2sh (1.99), 22.3sh (2.60), 27.5 (2.75)		8.56 (s, br), 7.08 (s, br)	8.4, 8.2
$(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$	DMSO	14.0 (3.14), 22.7 (3.17), 34.0 (4.03)	14.2	8.97 (AA′BB′), 6.63 (AA′BB′)	6.7, 3.3
K_3[**3**]$\cdot 5.5H_2O$	H_2O	21.8 (2.39), 28.9sh (2.87)	21.7	8.00 (AA′BB′), 6.86 (AA′BB′)	6.6, 4.9

[a] From Nujol mulls. [b] All amido proton peaks were broad singlets.

Table 4 ES mass spectral data[a]

Compound	m/z	Relative intensity	Fragment
K[**1**]·DMSO	371.0	2.40	[**1** + $2H_2O$]$^-$
	353.0	1.58	[**1** + H_2O]$^-$
	335.0	100	[**1**]$^-$
$(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$	700.0	23.32	[**2** + PPh_4]$^-$
	361.0	13.72	[**2** + H]$^-$
	180.5	100	[**2**]$^{2-}$
K_3[**3**]$\cdot 5.5H_2O$	418.0	6.85	[**3** − CN + K + H_2O]$^-$
	400.0	100	[**3** − CN + K]$^-$
	389.0	28.26	[**3** + 2H]$^-$
	194.0	0.58	[**3** + H]$^{2-}$
	180.4	56.52	[**3** − CN]$^{2-}$

[a] K[**1**]·DMSO and K_3[**3**]$\cdot 5.5H_2O$ in water; $(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$ in acetonitrile.

Table 5 Comparison of the bond lengths, absorption bands and ν(CN) stretching frequency of five-coordinate monocyano cobalt(III) complexes of the form $[Co^{III}(N_4)(CN)]^{n-}$

	Average bond lengths/Å			Absorption data			IR data
Equatorial N_4 ligand	Co–C	C–N	Co–N	$\sigma_{max}/10^3$ cm^{-1} (log {ε/dm^3 mol^{-1} cm^{-1}})			ν(CN)/cm^{-1}
bbphen^{4-}	1.821(7)	1.158(7)	1.887(5)	14.0 (3.14)	22.7 (3.17)	34.0 (4.03)	2114
$(C_4H_2N_4)_2{}^{2-}$ [a],[b]	1.859(6)	1.148(8)	1.874(5)	16.9 (3.79)	23.1 (3.50)	31.9 (4.67)	2100
taa^{2-},[c]	1.82(1)	1.16(2)	1.886(9)		27.5	37.7	2116

[a] $(C_4H_2N_4)_2{}^{2-}$ = Bis(diiminosuccinonitrile).[16] [b] Two independent molecules are present in the asymmetric unit. [c] taa^{2-} = dihydrobenzo[*b*,*i*][1,4,8,11]-tetraazacyclotetradecinato.[17]

The ^{13}C NMR spectra of the coordinated CN$^-$ were measured for $(PPh_4)_2$[**2**]$\cdot 2CH_3CN\cdot H_2O$ in DMSO-d_6 and K_3[**3**]$\cdot 5.5H_2O$ in D_2O. A broad ^{13}C signal without ^{59}Co–^{13}C coupling was observed for [**2**]$^{2-}$ at 81.5 ppm (linewidths, $\nu_{1/2}$ = 23.4 Hz) while [**3**]$^{3-}$ exhibits ^{13}CN signals at 143.0 ppm ($\nu_{1/2}$ = 61.6 Hz), similarly to the range 110 to 145 ppm observed for mixed cyano Co^{III} complexes[27] and to the chemical shift (140.0 ppm) for $K_3[Co(CN)_6]$.[28] The remarkable difference in the ^{13}C NMR chemical shifts between the di- and monocyano bbphen complexes may be accounted for by the following two factors. Firstly, as demonstrated for pentaammine[29] and pentacyano[28] Co^{III} complexes, the linear relationship was indicated between the ^{13}CN NMR chemical shift and the ligand-field parameters in terms of McConnels theoretical consideration; the contribution of the tetragonal components and the anisotropic nephelauxetic ratio [eqn. (1)].

$$\delta \propto \left\{ \frac{\beta[(N_{\text{biu}})_4]}{\alpha E(^1A_2)} - \frac{\beta[(N_{\text{biu}})_2(CN)_n]}{E(^1E_a)} \right\} \frac{(3\cos^2\theta - 1)}{3r_i^3} \qquad (1)$$

$$n = 2 \text{ for } [\mathbf{3}]^{3-} \text{ and } n = 1 \text{ for } [\mathbf{2}]^{2-}$$

The numerator $\beta[(N_{biu})_4]$ in the first term is the nephelauxetic ratio for $[Co(biuretato)_3]^{3-}$ and $\beta[(N_{biu})_2(CN)_2]$ in the second term is the weighted average of the nephelauxetic ratios for $[Co(biuretato)_3]^{3-}$ and $[Co(CN)_6]^{3-}$. The denominators $E(^1A_2)$ and $E(^1E_a)$ are the transition energies corresponding to the $^1A_2$ and $^1E_a \longleftarrow {}^1A_1$ components within the $Co(N_{biu})_4$ and $Co(N_{biu})_2(CN)_2$ planes. For [**2**]$^{2-}$ and [**3**]$^{3-}$, the first term $\beta[(N_{biu})_4]/E(^1A_2)$ is the same, as described before. On the other hand, the second term of [**2**]$^{2-}$ is larger than that of [**3**]$^{3-}$ because the denominator and numerator are smaller and larger, respectively, than those of [**3**]$^{3-}$. That is, $E(^1E_a)$ of [**2**]$^{2-}$ is predicted to be smaller than that of [**3**]$^{3-}$ on the basis of the comparison between the observed position and the AOM prediction, and the nephelauxetic ratio in the second term of [**2**]$^{2-}$ is represented as $\beta[(N_{biu})_2(CN)] = 1/4\{2\beta[(N_{biu})_6] + \beta[(CN)_6] + 1\}$ assuming that the nephelauxetic ratio for the void ligand in the monocyano complex is unity. On the basis of eqn. (1) therefore, the ^{13}CN chemical shift of [**2**]$^{2-}$ is predicted to be located at higher field than that of [**3**]$^{3-}$, as is observed. Secondly, the distinctive higher field chemical shift of the ^{13}CN signal for [**2**]$^{2-}$ is related to the Co–C distances; the Co–C bond length in [**2**]$^{2-}$, at 1.821(7) Å, is shorter than those in $[Co(CN)_6]^{3-}$ (1.896 Å)[30] and [**3**]$^{3-}$ [1.925(5) and 1.937(6) Å]. This indicates that the pπ–dπ interaction between the Co and CN$^-$ C atom in [**2**]$^{2-}$ is stronger than in the other complexes. Since the strong π-back bonding shields the CN$^-$ C atom, the ^{13}C NMR signal of [**2**]$^{2-}$ shifts to higher field.[31] These two structural and electronic factors cause the much higher field shift of the CN$^-$ signal for the five-coordinate complex.

Conclusions

The addition reaction of cyanide ion to complex [**1**]$^-$ afforded two complexes, [**2**]$^{2-}$ and [**3**]$^{3-}$, which were isolated as crystalline salts. Comparison of the solid and solution absorption spectra reveals that the structures of [**2**]$^{2-}$ and [**3**]$^{3-}$ are retained in solution. The X-ray analysis of [**2**]$^{2-}$ confirms a SPY-5 geometry for the complex. Systematic bond length variations are observed among the four-, five- and six-coordinate (bbphen) complexes, according to the bond variation rule. The cyano ^{13}CN NMR signal of [**2**]$^{2-}$ is distinctively shifted to higher field, which can be explained by considering the electronic and structural characteristics of the five-coordinate Co^{III} complex.

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