4786 reflections
207 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2 + 0.8546P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Si1—C19$^{\rm i}$	1.866 (2)	Sn1—C6	2.161 (2)
Si1—C3	1.869 (2)	Si2—C6	1.865 (2)
Sn1—C3	2.161 (2)	Si2—C12	1.865 (2)
C19$^{\rm i}$—Si1—C3	108.59 (9)	Sn1—C6—Si2	115.6 (1)
Si1—C3—Sn1	118.0 (1)	C6 Si2—C12	111.5 (1)
C3—Sn1—C6	111.50 (8)		

Symmetry code: (i) $1 - x, -y, -z$.

All H atoms were located in the difference Fourier map, but were placed in calculated positions using a riding model and refined with common isotropic displacement parameters for different C—H types [methylene C—H 0.97 Å and $U_{\rm iso}$ 0.058 (2) Å^2; methyl C—H 0.96 Å and $U_{\rm iso}$ 0.058 (2) Å^2; aromatic C—H 0.93 Å and $U_{\rm iso}$ 0.043 (3) Å^2].

Data collection: Nonius MACH3 Argus software. Cell refinement: Nonius MACH3 Argus software. Data reduction: *CORINC* (Dräger & Gattow, 1971). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

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An Adduct Between Tetraammine(1,10-phenanthroline)ruthenium(II) and Dibenzo-42-crown-14

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Abstract

The crystal structure of the adduct dibenzo-42-crown-14 (*OC*-6-22)-tetraammine(1,10-phenanthroline-*N*,*N*′)-ruthenium(II) bis(hexafluorophosphate) dichloromethane solvate, $[\mathrm{Ru(C_{12}H_8N_2)(NH_3)_4](PF_6)_2.C_{36}H_{56}O_{14}.CH_2Cl_2}$, is reported. The guest Ru complex is located deep within the U-shaped cavity formed by folding of the flexible crown host. The ammine ligands of the Ru complex participate in an extensive network of hydrogen bonds with the ether O atoms of the crown. Weak π stacking appears to occur between the aromatic rings of the phenanthroline ligand and the benzene groups of the crown ether.

Comment

Hydrogen-bonding interactions between crown O atoms and ammine protons play an important role in the molecular recognition of ammine–metal complexes by crown ethers. For a recent list of references on this subject, see Zhang *et al.* (1994); for earlier references, see Colquhoun *et al.* (1986). We have observed that binding of ruthenium–ammine complexes by large cyclic crown ethers increases with the size

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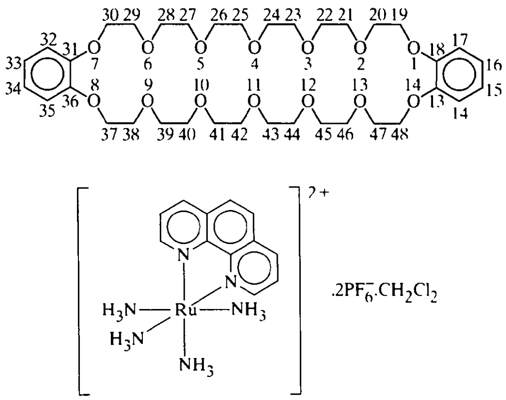
and flexibility of the crown host, increased availability of ammine ligands, and a higher oxidation state of the Ru metal center (Todd *et al.*, 1993; Zhang *et al.*, 1995). NMR NOE (nuclear Overhauser enhancement) studies of $[Ru(NH_3)_4(bpy)]^{2+}$.[DB-42-CR-14] (bpy is 2,2′-bipyridine and DB-42-CR-14 is dibenzo-42-crown-14) indicated a coplanar arrangement of the benzene groups of the crown host, which are centered over the aromatic rings of the bpy ligand. Similar arrangements of dibenzo–crown adducts with $[Pt(NH_3)_2(bpy)]^{2+}$ and with organic bpy derivatives are well documented (see below). The association constant between $[Ru(NH_3)_4(phen)]^{2+}$ (phen = 1,10-phenanthroline) and the large DB-42-CR-14 host was particularly high and we set out to investigate the solid-state structure of this adduct, (I).



(I)

An *ORTEP* (Johnson, 1965) drawing of the metal complex is shown in Fig. 1. Numbering of the crown ether host is shown schematically above. The bond lengths and angles associated with the Ru center (Table 1) and the crown host are normal, with Ru—NH_3 and Ru—N_{phen} bond lengths of 2.120 (4)–2.145 (4) and 2.023 (4)–2.029 (4) Å, respectively. Pentaammine-Ru^{II} complexes typically have Ru—NH_3 bonds of ~2.10–2.17 Å (Graves & Hodgson, 1979; Gress *et al.*, 1981; Crutchley *et al.*, 1990; Chou *et al.*, 1994), and $[Ru(bpy)_3]^{2+}$ has Ru—N bonds ranging from 2.04 to 2.07 Å (Biner *et al.*, 1992; Rillema *et al.*, 1992; Harrowfield & Sobolev, 1994; Tamura *et al.*, 1996; Krausz *et al.*, 1995; Turner *et al.*, 1995). As shown in Fig. 2, the $[Ru(NH_3)_4(phen)]^{2+}$ cation guest sits in a cavity formed by the crown host, which adopts a folded U-shaped conformation, the benzene rings from the host being located at the edges of the crown cavity. The ammine ligands from the Ru complex sit deep in the host, where they form hydrogen bonds with the ether O atoms from the crown.

An extensive network of N—H···O bonds is present between the complex cation and the crown host (Fig. 2).

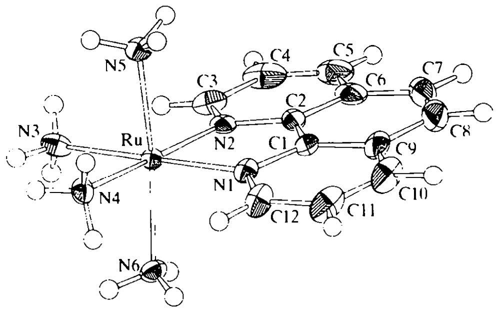


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the $[Ru(NH_3)_4(phen)]^{2+}$ cation, along with the numbering scheme. Displacement ellipsoids are represented at the 50% probability level.

Geometric parameters related to hydrogen bonding are shown in Table 2. Each crown O atom is an acceptor to one ammine ligand on the Ru atom, except for O3 and O5, which are acceptors to two ammine ligands. The N4 ammine ligand is donor to the four crown O atoms (O4, O10–O12) located farthest from the benzene groups in the polyether chain (see Scheme for the numbering of the crown). The ligand associated with N5 is donor to five crown O atoms (O5–O9) near one of the benzene rings, while the ammine ligand associated with N6 forms hydrogen bonds with the corresponding O atoms (O1–O3, O13, O14) in the aliphatic chain close to the other benzene. The N···O distances for these contacts range from 2.975 (5) to 3.299 (5) Å. Second-sphere complexes between ammine–metal complexes

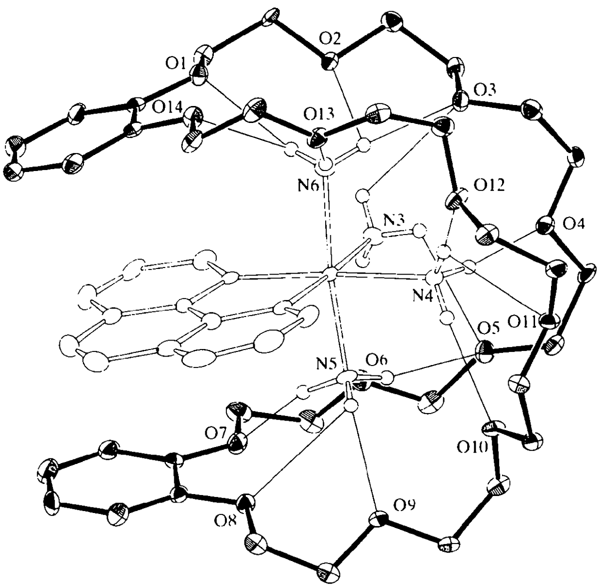


Fig. 2. Hydrogen bonding of the ammine ligands with the crown O atoms. The ammine ligand associated with N3 is also donor to an F atom (not shown) of a PF_6^- species. Non-ammine H atoms have been omitted for clarity. Displacement ellipsoids are represented at the 30% probability level.

and crown ethers often exhibit long hydrogen bonds in this range, with N···O separations of *ca* 3.0–3.4 Å (Colquhoun *et al.*, 1986). The remaining ammine ligand forms a hydrogen bond with one of the PF_6^- species [N3···F3 = 3.145 (5) Å], and with O3 and O5 [N3···O = 3.299 (5) and 3.085 (5) Å, respectively], two ether O atoms already participating in hydrogen bonding with N6 and N5. A similar N—H···F bond (3.20 Å) has been reported in the host–guest complex [DB-30-CR-10].$[Pt(NH_3)_2(bpy)]^{2+}$ (Colquhoun *et al.*, 1981).

The phen ligand and the benzene rings from the dibenzo–crown host are all roughly parallel to one another. The dihedral angle between the planes of the benzenes in the crown is 19.3 (2)°. As shown in Fig. 3, the six-membered rings of the two benzo groups are almost perfectly aligned, so that each aromatic C atom within the host fragment is located directly above another aromatic (host) C atom, at a distance of 6.5–7.4 Å. The shortest non-bonded contacts between the benzo groups of the host and the phen ligand of the guest are found between the C5 atom of the phen and the C16 and C32 atoms of the benzene ring [C5···C16 = 3.339 (8) and C5···C32 = 3.303 (7) Å]. The dihedral angles between the mean least-squares plane of the phen ligand and each of the two crystallographically independent benzene groups in the crown are 7.7 (1) and 13.1 (1)°. Other adducts between benzo–crown derivatives (ring size = 30–34) and $[Pt(NH_3)_2(bpy)]^{2+}$, or organic guests derived from 2,2′-bpy or 4,4′-bpy, also feature a quasi-parallel alignment of the benzene rings of the host and the polypyridyl moiety of the guest (Colquhoun *et al.*, 1981, 1986; Kohnke *et al.*, 1985; Allwood *et al.*, 1985, 1987*a*,*b*; Allwood, Colquhoun *et al.*, 1987; Allwood, Shahriari-Zavareh *et al.*, 1987; Ashton *et al.*, 1987). Host–guest aromatic ring separations are typically 3.2–3.7 Å, with the distance between the benzene rings in the host ranging from 6.8 to 7.0 Å, and with deviations from parallel alignment of the benzene groups in the host amounting to *ca* 1–10°. In view of these results, the title structure presents π contacts between the phen ligand and the benzene groups which are within the normal range. Although larger than usually observed, the 19.3° dihedral angle between the planes of the benzene rings is not unprecedented. This angle has been reported to be as large as 22° in a [dinaphtho-30-crown-10].-$[Pt(NH_3)_2(bpy)]^{2+}$ adduct (Allwood, Colquhoun *et al.*, 1987).

All torsion angles about the aliphatic C—C bonds adopt a *gauche* conformation (torsion angle of ± *ca* 65°), while those angles about C—O bonds are mostly *trans* (within *ca* 30° of 180°), with some C—C—O—C angles adopting a *gauche* conformation. There is little doubt that it is this flexibility in the polyether chain that allows the crown host to adopt an optimal conformation, which maximizes both hydrogen bonding between the ammine ligands and the ether O atoms, and π-stacking between the aromatic rings of the Ru complex guest and the dibenzo–crown host.

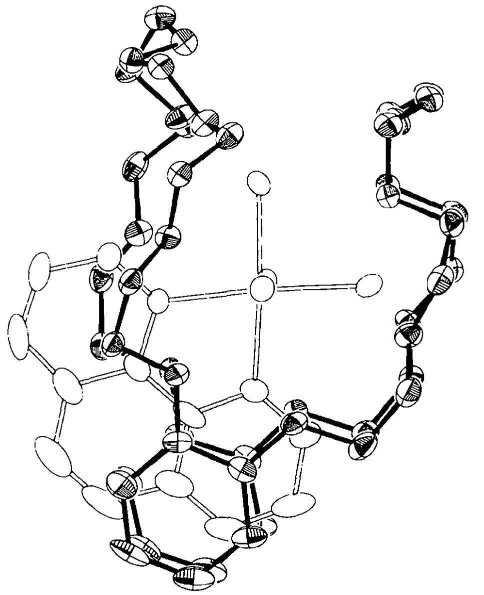


Fig. 3. *ORTEP* (Johnson, 1965) drawing of the $[Ru(NH_3)_4(phen)]^{2+}$.-DB-42-CR-14 adduct, showing the overlap between the phenanthroline ligand and the benzene groups on the crown. The complex cation is represented with hollow ellipsoids and the crown ether with shaded octants. H atoms have been omitted for clarity. Displacement ellipsoids are represented at the 50% probability level.

Experimental

$[Ru(NH_3)_4(phen)](PF_6)_2$ was prepared as described by Curtis *et al.* (1983) for the 2,2′-bipyridine analog. The synthesis of DB-42-C-14 is reported elsewhere (Todd *et al.*, 1993). Hexanes (13 ml) were layered on top of a solution of $[Ru(NH_3)_4(phen)](PF_6)_2$ (21.5 mg, 0.034 mmol) and DB-42-C-14 (24 mg, 0.034 mmol) in 7 ml of dry CH_2Cl_2. Needles of the adduct (31 mg, 68% yield) were isolated after 5 d in the refrigerator.

Crystal data

$[Ru(C_{12}H_8N_2)(NH_3)_4]$-
$(PF_6)_2.C_{36}H_{56}O_{14}.CH_2Cl_2$
M_r = 1437.09
Triclinic
$P\bar{1}$
a = 11.479 (2) Å
b = 12.828 (2) Å
c = 22.475 (3) Å
α = 89.04 (1)°
β = 84.80 (1)°
γ = 69.19 (1)°
V = 3080.4 (8) Å^3
Z = 2
D_x = 1.547 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 9.0–11.6°
μ = 0.494 mm^{-1}
T = 153 (2) K
Needle
0.32 × 0.20 × 0.05 mm
Purple

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
T_{min} = 0.867, T_{max} = 0.970
8803 measured reflections
8545 independent reflections
5945 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 22.97°
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 24$
3 standard reflections every 90 reflections intensity decay: 1.6%

Refinement

Refinement on F^2
$R(F)$ = 0.047
$wR(F^2)$ = 0.081
S = 1.89
8545 reflections
776 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 1.05 e Å^{-3}
$\Delta\rho_{min}$ = −1.51 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 3.1 (14) × 10^{-8}
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ru—N1	2.023 (4)	Ru—N4	2.127 (4)
Ru—N2	2.029 (4)	Ru—N5	2.120 (4)
Ru—N3	2.145 (4)	Ru—N6	2.130 (4)
N1—Ru—N2	80.52 (16)	N2—Ru—N6	94.95 (15)
N1—Ru—N3	175.84 (16)	N3—Ru—N4	88.23 (14)
N1—Ru—N4	95.85 (15)	N3—Ru—N5	88.51 (14)
N1—Ru—N5	92.49 (15)	N3—Ru—N6	87.59 (14)
N1—Ru—N6	91.77 (15)	N4—Ru—N5	86.74 (14)
N2—Ru—N3	95.43 (15)	N4—Ru—N6	88.03 (14)
N2—Ru—N4	175.36 (16)	N5—Ru—N6	173.57 (15)
N2—Ru—N5	90.51 (14)		

Table 2. *Hydrogen-bonding geometry (Å)*

D—H···*A*	*D*···*A*
N3—H65···F3^{i}	3.146 (5)
N3—H66···O3	3.299 (5)
N3—H67···O5	3.085 (5)
N4—H68···O4	2.988 (5)
N4—H69···O12	2.975 (5)
N4—H70···O10	3.147 (5)
N4—H69···O11	3.223 (5)
N5—H71···O9	3.064 (5)
N5—H72···O5	3.108 (5)
N5—H73···O7	3.190 (5)
N5—H72···O6	3.239 (5)
N5—H71···O8	3.097 (5)
N6—H74···O3	3.114 (5)
N6—H75···O1	3.134 (5)
N6—H76···O13	3.084 (5)
N6—H74···O2	3.111 (5)
N6—H75···O14	3.099 (5)

Symmetry code: (i) $-x, 1-y, 1-z$.

Data were only collected up to θ = 23°, because of the low intensities of the reflections. H atoms on the crown and phen fragments were calculated at idealized positions using a riding model, with C—H bonds of 0.95 Å and displacement parameters 20% larger than that of the corresponding C atom. The H atoms on the ammine ligands were located from a Fourier map. The number of observed reflections did not allow for refinement of all atomic postions. Therefore, the positions of the ammine H atoms were not refined, and their isotropic displacement parameters were fixed at a value 50% larger than that of their bonded N atom. Two F atoms (F2 and F6) of one of the PF_6^- anions showed large displacement ellipsoids. These are probably associated with unresolved disorder, but attempts to model the disorder were not successful. The largest residual peak (1.05 e Å^{-3}) in the difference Fourier map is located between two F atoms (F9 and F12) of the PF_6^- counter-ion associated with P2. No other peaks of significant intensity were found around P2. The largest negative peak (−1.51 e Å^{-3}) is located 0.09 Å from the Ru atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1387). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1431–1435

Poly[bis(benzimidazole-N^3)copper(II)-μ-acetylenedicarboxylato-O:O'-μ-aqua] and Poly[bis(benzimidazole-N^3)copper(II)-μ-aqua-μ-fumarato-O:O']

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Abstract

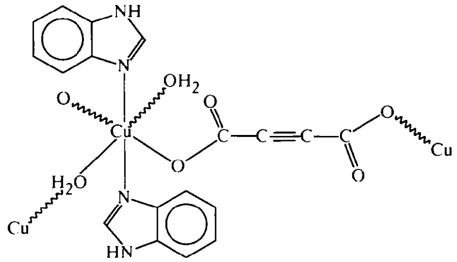
The title compounds, poly[bis(benzimidazole-N^3)-copper(II)-μ-acetylenedicarboxylato-O:O'-μ-aqua], $[Cu(C_4O_4)(C_7H_6N_2)_2(H_2O)]$, (I), and poly[bis(benzimidazole-N^3)copper(II)-μ-aqua-μ-fumarato-O:O'], $[Cu(C_4H_2O_4)(C_7H_6N_2)_2(H_2O)]$, (II), have been synthesized and their crystal structures determined by single-crystal X-ray diffraction at room temperature. Structures (I) and (II) are very similar. In both structures, the centrosymmetric Cu atoms are bridged by the dicarboxylic acid ions in a bis-monodentate fashion, forming polymeric chains. The Cu···Cu intrachain distances are 9.546 (1) Å in (I) and 9.276 (1) Å in (II). These chains are connected by bridging H_2O molecules, which are located on the twofold axes by Cu–H_2O bonds of 2.593 (1) Å in (I) and 2.668 (1) Å in (II). The Cu···Cu distances in the –Cu–H_2O–Cu– chains are 5.090 (1) and 5.199 (1) Å in (I) and (II), respectively. The base of the elongated octahedron of the Cu^{II} atoms is formed by two short Cu—O and two short Cu—N bonds [Cu—O = 1.970 (1) and 1.946 (2) Å, and Cu—N = 2.005 (2) and 2.016 (2) Å in (I) and (II), respectively]. The coordination of the carboxylate groups and the hydrogen bonds are discussed. The isostructurality of the title compounds and of their previously investigated homologue, (III), has been analysed.

Comment

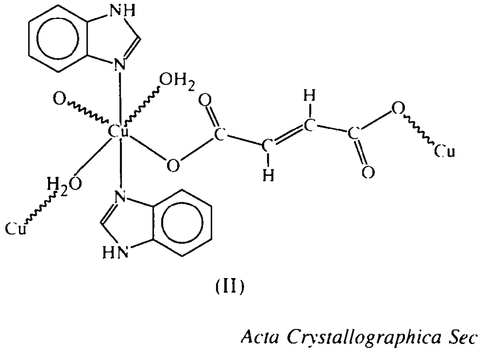
The Cu^{II} complexes of dicarboxylic acids are of interest because of their rich variety of structural features and their interesting magnetic properties. Most often, the Cu atoms are bridged by the dicarboxylic acid ions in a bis-bidentate fashion (Tosik *et al.*, 1995*a*), and rarely in the chelate-bridge tridentate fashion (Tosik *et al.*, 1995*b*) or the bis-bridge monodentate fashion (Tosik & Bukowska-Strzyżewska, 1992).

A knowledge of the structure is needed to allow an interpretation of the magnetic properties of polynuclear complexes with paramagnetic centres. It has been shown that two paramagnetic centres could interact through extended bridging ligands, even if these centres were relatively far away from each other (Verdaguer *et al.*, 1984).

The bridging acetylenedicarboxylato and fumarato ligands in the title compounds, (I) and (II), give a Cu···Cu separation of less than 10 Å, and the present μ-aqua Cu^{II} complexes provide an opportunity for analysing the interaction between neighbouring Cu^{II} centres through the apical water molecules. The magnetic properties of the title compounds will be investigated at a later date.



(I)



(II)

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