A macrobicyclic Ag^{I}_{3} cage encapsulating two cobalt(III) ions: synthesis, structure and reactivity

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Reaction of the S-bridged $Co^{III}_2Ag^{I}_3$ pentanuclear complex, $[Ag^{I}_3\{Co^{III}(aet)_3\}_2]^{3+}$ (1; aet = $NH_2CH_2CH_2S^-$), with paraformaldehyde in basic acetonitrile, followed by adding aqueous ammonia, produces the aza-capped complex, $[Ag^{I}_3\{Co^{III}(L)\}_2]^{3+}$ [2; L = $N(CH_2NHCH_2CH_2S^-)_3$] , in which two Co^{III} atoms are encapsulated in a macrobicyclic cage consisting of two aza-capped ligands L and three Ag^{I} atoms; 2 is converted to the aza-capped $Co^{III}_4Zn^{II}_4$ octanuclear complex, $[Zn^{II}_4O\{Co^{III}(L)\}_4]^{6+}$, by the reaction with I^- in the presence of ZnO and Zn^{2+} in water, retaining the chiral configuration of the aza-capped $[Co^{III}(L)]$ units.

Since the discovery of the formation of the aza-capped cage complex, $[Co(sepulchrate)]^{3+}$, by the facile condensation of formaldehyde and ammonia with $[Co(en)_3]^{3+}$ (en = $NH_2CH_2CH_2NH_2$),[1] similar preparative techniques have been applied to obtain analogous metal complexes with a macrobicyclic cage, which exhibit unique stereochemical and redox properties.[2–10] The cage complexes of this type have been derived from mononuclear metal complexes and thus contain only one metal ion. In order to expand the co-ordination chemistry of metal ions encapsulated in a macrobicyclic cage, it is desirable to introduce two or more metal ions in one cage. We report here the synthesis and structure of a new class of macrobicyclic cage complex encapsulating two cobalt(III) ions, $[Ag_3\{Co(L)\}_2]^{3+}$ [L = $N(CH_2NHCH_2CH_2S^-)_3$], together with its conversion to the $Co^{III}_4Zn^{II}_4$ octanuclear complex, $[Zn_4O\{Co(L)\}_4]^{6+}$.

Treatment of a dark purple acetonitrile solution of the S-bridged $Co^{III}_2Ag^{I}_3$ pentanuclear complex, $[Ag_3\{Co(aet)_3\}_2](BF_4)_3\cdot H_2O$ [**1**$(BF_4)_3\cdot H_2O$; aet = $NH_2CH_2CH_2S^-$],[11] with paraformaldehyde and triethylamine at room temperature gave a dark red solution, which turned dark purple upon the addition of aqueous ammonia. A dark purple powder [**2**$(NO_3)_3\cdot 4H_2O$] was isolated from the dark purple reaction solution by adding an aqueous solution of $NaNO_3$ (80% yield).‡ The absorption spectrum of **2** is quite similar to that of **1** over the whole region. In the ^{13}C NMR spectrum **2** gives three sharp signals at δ 34.64, 61.62, and 69.76, which is distinct from the two ^{13}C NMR signals at δ 36.64 and 51.41 observed for **1**.[11] From these facts and elemental analysis, it is assumed that **2** has an aza-capped $Co^{III}_2Ag^{I}_3$ pentanuclear structure in $[Ag_3\{Co(L)\}_2]^{3+}$ [L = $N(CH_2NHCH_2CH_2S^-)_3$]. **2** was optically resolved into its enantiomers, $(+)^{CD}_{580}$ and $(-)^{CD}_{580}$, by SP-Sephadex C-25 column chromatography using $[Sb_2(R,R\text{-tartrato})_2]^{2-}$ as eluent. The CD spectrum of $(-)^{CD}_{580}$-**2** corresponds well with that of the $\Delta\Delta$ isomer of **1**, which implies that the two [Co(L)] units in $(-)^{CD}_{580}$-**2** have the Δ configuration.

The structure of **2** was established by a single crystal X-ray analysis of the PF_6^- salt [**2**$(PF_6)_3\cdot H_2O$], which was prepared by adding an aqueous solution of $NaPF_6$ to the aqueous solution of **2**$(NO_3)_3\cdot 4H_2O$.§ The total occupancy factor of the PF_6^- anions implies that the entire complex cation **2** is trivalent. As shown in Fig. 1, the entire complex cation **2** contains two Co^{III} and three Ag^{I} atoms. Each Co^{III} atom is surrounded by an aza-capped hexadentate N_3S_3 ligand L to form an approximately octahedral $[Co^{III}(L)]$ unit. The two $[Co^{III}(L)]$ units are spanned by three Ag^{I} atoms, such that the three S–Ag–S linkages form a triple helical structure. As a result, the two Co^{III} atoms are encapsulated in a macrobicyclic metallo-cage, $[Ag^{I}_3(L)_2]^{3-}$, in which each of three Ag^{I} atoms is linearly coordinated by two S atoms from two aza-capped ligands L. Except for the presence of the two terminal aza caps, the overall structure of **2** is similar to that of the parent complex **1**.[11] In particular, the bond distances and angles around the Co^{III} atoms in **2** [average Co–S = 2.243(8) Å, Co–N = 2.02(3) Å, S–Co–S = 91.3(3)°, N–Co–N = 89(1)°] are in good agreement with those in **1** [average Co–S = 2.248(8) Å, Co–N = 2.03(3) Å, S–Co–S = 92.1(3)°, N–Co–N = 90(1)°]. However, the averaged Ag–S distance in **2** [2.417(8) Å] is *ca.* 0.04 Å longer than that found in **1** [2.378(8) Å]. Moreover, the S–Ag–S angles [average 177.9(4)°] in **2** are closer to 180° than those in **1** [average 174.6(3)°], which permits the slightly shorter Ag···Ag separations in **2** [average 2.956(4) Å], compared with the separations in **1** [average 3.029(3) Å].

The two [Co(L)] units in **2** have the same chiral configuration to form the $\Delta\Delta$ and $\Lambda\Lambda$ isomers; the former isomer is illustrated in Fig. 1. This is compatible with the fact that **2** was optically resolved into its enantiomers. In the crystal lattice the $\Delta\Delta$ and $\Lambda\Lambda$ isomers co-exist in a disordered manner with a site occupancy of 0.5, which indicates that crystal **2** is not a racemic compound but a solid solution.[12] All the six bridging S atoms are fixed to the *S* configuration for the $\Delta\Delta$ isomer and *R* for the $\Lambda\Lambda$ isomer. The helical structure due to three S–Ag–S linkages is left-handed for the $\Delta\Delta$ isomer and right-handed for the $\Lambda\Lambda$ isomer. These stereochemical properties are the same as those in **1**.[11] However, it should be noted that in **2** all the five-membered N,S-chelate rings adopt the *lel* conformation, which is in contrast to the fact that the *ob* conformation as well as the *lel* one has been found in **1**. All the six asymmetric N atoms in **2** have the *R* configuration for the $\Delta\Delta$ isomer and *S* for the $\Lambda\Lambda$ isomer.

Attempts to fit the S-bridged $Co^{III}_4Zn^{II}_4$ octanuclear complex, $[Zn_4O\{Co(aet)_3\}_4]^{6+}$,[13] with aza caps by a similar condensation reaction were unsuccessful, because of the decomposition of $[Zn_4O\{Co(aet)_3\}_4]^{6+}$ in basic conditions. Instead, the corresponding aza-capped complex, $[Zn^{II}_4O\{Co^{III}(L)\}_4]^{6+}$ (**3**), was successfully derived from **2** (Scheme 1). That is, treatment of **2** with a stoichiometric amount of NaI in the presence of excess ZnO and $Zn(NO_3)_2\cdot 6H_2O$ in water at

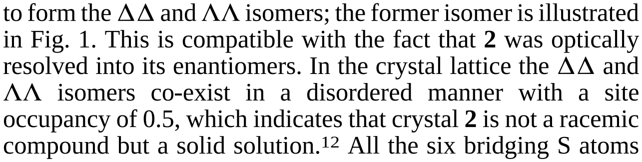
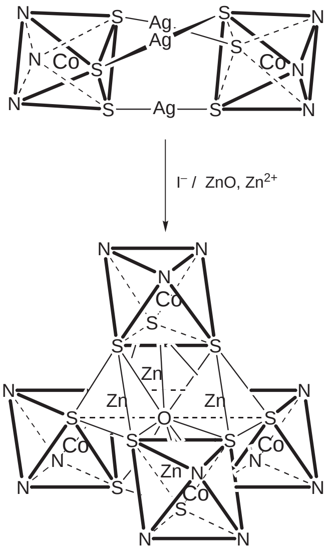


Fig. 1 A perspective view of the complex cation **2** (the $\Delta\Delta$ isomer) with the atomic labeling scheme. The overlapped $\Lambda\Lambda$ isomer is omitted for clarity



2

3

Scheme 1 Conversion of the $Co^{III}_2Ag^{I}_3$ pentanuclear structure in **2** to the $Co^{III}_4Zn^{II}_4$ octanuclear structure in **3**

room temperature gave a dark blue–purple solution, from which a black powder [**3**$(ClO_4)_6\cdot 7H_2O$] was isolated by adding an aqueous solution of $NaClO_4$ (50% yield).¶Compound **3** was characterized by (i) elemental and plasma emission spectral analyses, (ii) electronic absorption spectroscopy, the spectral features of which coincide well with that of $[Zn_4O\{Co(aet)_3\}_4]^{6+}$, and (iii) ^{13}C NMR spectroscopy which gives three sharp signals at δ 32.63, 61.15, and 69.51. The cyclic voltammogram of **3** at a glassy-carbon electrode in a 0.2 mol dm^{-3} aqueous $NaNO_3$ solution yields four consecutive redox couples ($E = -0.43, -0.55, -0.62$, and -0.75 V *vs*. Ag/AgCl, 100 mV s^{-1}). Similar redox behavior is characteristically observed for $[M_4O\{Co(aet)_3\}_4]^{6+}$ (M = Zn, Hg) having a *T*-symmetrical $Co^{III}_4M^{II}_4$ octanuclear structure.[13,14] Thus, it is confirmed that **3** has the S-bridged $Co^{III}_4Zn^{II}_4$ octanuclear structure in $[Zn^{II}_4O\{Co^{III}(L)\}_4]^{6+}$. Compound **3** was optically resolved into its enantiomers, $(+)^{\mathrm{CD}}_{580}$ and $(-)^{\mathrm{CD}}_{580}$, by SP-Sephadex C-25 column chromatography. Since the CD spectrum of $(-)^{\mathrm{CD}}_{580}$-**3** is very similar to that of the $\Delta\Delta\Delta\Delta$ isomer of $[Zn_4\{Co(aet)_3\}_4]^{6+}$, it is assumed that the four [Co(L)] units in $(-)^{\mathrm{CD}}_{580}$-**3** have the Δ configuration. When $\Delta\Delta$-**2** was used as the starting complex, instead of the racemate of **2**, only the $\Delta\Delta\Delta\Delta$ isomer of **3** was formed. This result indicates that the $Co^{III}_2Ag^{I}_3$ pentanuclear structure in **2** is converted to the $Co^{III}_4Zn^{II}_4$ octanuclear structure in **3** with retention of the chiral configuration of the [Co(L)] unit. Similar conversion reactions of **2** to other S-bridged polynuclear structures are currently under way.

Notes and References

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‡ Anal. Calc. for **2**$(NO_3)_3\cdot 4H_2O$ = $C_{18}H_{50}Ag_3Co_2N_{11}O_{13}S_6$: C, 17.12, H; 3.99; N, 12.20; Co, 9.34; Ag, 25.63. Found: C, 17.05; H, 3.78; N, 12.25; Co, 9.28; Ag, 25.63%. VIS–UV spectrum in H_2O [$\nu/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})]: 17.54 (2.97), 23.5 sh (2.90), 36.36 (4.62), 37.9 sh (4.6). The sh label denotes a shoulder. CD spectrum in H_2O [$\nu/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})]: 17.73 (−16.36), 22.62 (+21.72), 25.71 (−13.25), 30.12 (+14.77), 36.76 (−129.22), 42.92 (+83.04). ^{13}C NMR (500 MHz, D_2O, ppm from DSS): δ 34.64 (CH_2S), 61.62 ($NHCH_2$), 69.76 (NCH_2NH) (DSS = 4,4′-dimethyl-4-silapentane-1-sulfonate).

§ Anal. Calc. for **2**$(PF_6)_3\cdot H_2O$ = $C_{18}H_{44}Ag_3Co_2F_{18}N_8OP_3S_6$: C, 14.83, H; 3.04; N, 7.69. Found: C, 15.13; H, 3.03; N, 7.73%. *Crystal data* for **2**$(PF_6)_3\cdot H_2O$: $C_{18}H_{44}Ag_3Co_2F_{18}N_8OP_3S_6$, M = 1457.3, tetragonal, space group $I42m$ (no. 121), a = 13.012(1), c = 24.707(2) Å, U = 4182.8(8) $Å^3$, Z = 4, μ(Mo-Kα) = 26.81 cm^{-1}, 1413 unique reflections at 296 K, R = 0.055 for 1025 reflections with $I > 1.5\sigma(I)$. For the atoms of the complex cation, Co(1), Ag(1), N(4), C(3) and C(4) were constrained to the special positions of symmetry *m* with a site occupancy factor of 0.5, while Ag(2) was constrained to the position of symmetry 2*mm* with a site occupancy factor of 0.25. The site occupancy factor of other atoms of the complex cation, except C(1) and C(2), was fixed to 0.5. The symmetry-expansion operation showed that a pair of enantiomers co-exist in each of four sites in the unit cell, sharing the C atoms of the N,S-chelate rings, besides the Ag, Co and aza-capped N atoms. CCDC 182/923.

¶ Anal. Calc. for **3**$(ClO_4)_6\cdot 7H_2O$ = $C_{36}H_{98}Cl_6Co_4N_{16}O_{32}S_{12}Zn_4$: C, 18.31, H;4.18; N,9.49; Co, 9.98; Zn, 11.07. Found: C, 18.16; H, 4.24; N, 9.76; Co, 10.25; Zn, 11.45%. VIS–UV spectrum in H_2O [$\nu/10^3$ cm^{-1} (log ε/mol^{-1} dm^3 cm^{-1})]: 17.54 (3.31), 23.41 (3.41), 29.87 (4.32), 37.31 (4.94). CD spectrum in H_2O [$\nu/10^3$ cm^{-1} ($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})]: 17.18 (−19.44), 21.82 (+8.83), 26.68 (+12.40), 34.60 (−111.75), 39.52 (+120.15), 43.67 (+143.24). ^{13}C NMR (500 MHz, D_2O, ppm from DSS): δ 32.63 (CH_2S), 61.15 ($NHCH_2$), 69.51 (NCH_2NH).

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Received in Cambridge, UK, 30th April 1998; 8/03257B