

The rediscovery of Alfred Werner's second hexol†

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A compound originally prepared by Alfred Werner but structurally misassigned has been shown by three independent X-ray structural analyses to be a hexanuclear species which can now be regarded as Werner's second hexol, his first being that famous for being the first non-carbon containing species to be optically resolved.

Alfred Werner received the Nobel Prize in 1913 before perhaps his most significant individual discovery, the optical resolution of the first non-carbon containing substance, a result published in the same year.¹ This material, originally synthesised by Jørgensen was Werner's famous 'hexol' (Fig. 1), which we dub his first hexol.

In 1983 a conference paper was presented² describing the structural characterisation (Fig. 2) of another hexol, a hexanitrate·4H₂O salt,[§] and a very minor by-product of the synthesis of Fremy's salt, [(NH₃)₅Co–O₂–Co(NH₃)₅](NO₃)₄.^{3,4} This structure was not published in the open literature because the data were lost in an accident, and the synthesis could not be reproduced.

Some 15 years later a complex believed by Werner to be the hexol shown in Fig. 3 was synthesised according to Werner's original directions,^{5,6} but its properties (*vide infra*) could not be reconciled with Werner's original formulation. The material was

obtained as a green side-product from the filtrates of solutions which had yielded the red triol, [(NH₃)₃Co(μ–OH)₃Co(NH₃)₃]Cl₃, as the major product. The essential procedure involved basification of a solution of *fac*- or *mer*-[Co(NH₃)₃(OH)₂]₃³⁺.

As part of a study of the ¹H NMR spectra of a range of bridging OH[–] and NH₂[–] di- and poly-nuclear Co(III) complexes,^{7,8} most of which had been originally synthesised by Werner, the spectrum (Fig. 4) was recorded for Werner's supposed trinuclear hexol, Fig. 3.¶ The expected singlet for the 18 equivalent NH₃ protons, and another singlet for the six equivalent OH protons at very high field (well above SiMe₄), were not observed. Instead, a lower symmetry complex was apparent, but one clearly bearing the high field bridging OH protons. We suspected this material was actually that shown in Fig. 2 and that we had discovered a reproducible synthesis for it, *i.e.*, that described^{5,6} by Werner.

This olive brown product was purified by ion-exchange chromatography on Sephadex using 2 M NH₄Cl as eluant. On reducing the volume of the eluate for the slowest moving green band and adding ZnCl₂ and methanol, deep olive green crystals were obtained. This material did not analyse well, and under the microscope two crystal modifications were apparent—small deep green blocks and larger khaki colored needles. The ¹H NMR spectrum, however, was the same for each, and they eluted together on Sephadex, and thus it seems likely the materials differ only in the constitution of the counterions. When spiked with Werner's original grey-black 6+ hexol (Fig. 1), the complexes eluted together, consistent with the common 6+ charge (Werner's formulation involves a 3+ ion); the 3+ complex [(NH₃)₃Co(μ–OH)₂(di-μ–NH₂)Co(NH₃)₃]³⁺ was used as a marker and it eluted well ahead of the two hexols.

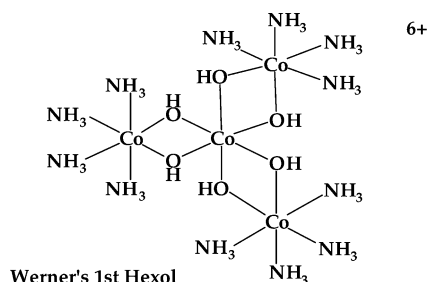


Fig. 1

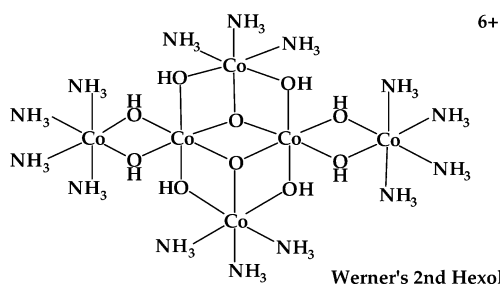


Fig. 2

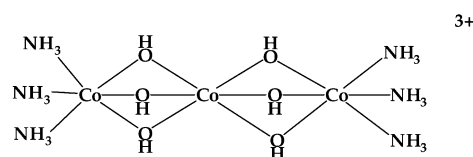
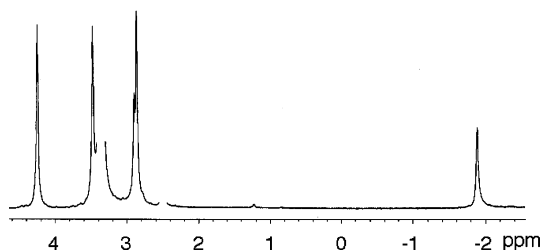


Fig. 3

Fig. 4 ¹H NMR spectrum of [Co₆(NH₃)₁₄(OH)₈(O)₂]⁶⁺ in Me₂SO-*d*₆.† Electronic supplementary information (ESI) available: effect of mild acid on the second hexol. See <http://www.rsc.org/suppdata/cc/b4/b408277j/>

‡ Deceased.

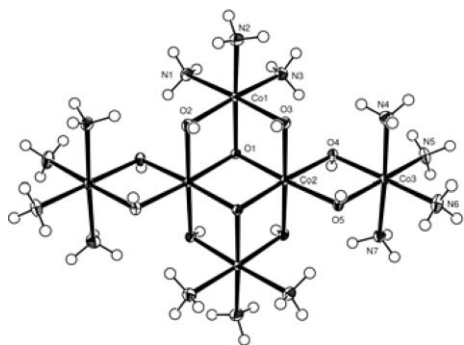


Fig. 5 The molecular cation $[\text{Co}_6(\text{NH}_3)_{14}(\text{OH})_8(\text{O})_2]^{6+}$, showing 20% anisotropic displacement parameters. Selected bond lengths (Å) and angles($^\circ$): Co(2)–O(1) 1.8871(14); Co(1)–O(1) 1.9056(14); Co(2)–O(2)H 1.8975(15); Co(1)–O(2)H 1.9050(15); Co(1)–O(3)H 1.9000(15); Co(2)–O(4) 1.9309(15); Co(2)–O(5) 1.9322(15); Co(3)–N(4) 1.9550(20); Co(3)–N(7) 1.9331(19); Co(2)–O(1)–Co(2) 95.90(7); O(1)–Co(2)–O(1) 84.10(7); O(3)–Co(2)–O(1) 95.62(6); O(2)–Co(2)–O(1) 94.79(6).

The dark green blocks diffracted well, and the single crystal X-ray structural analysis was therefore undertaken on this material which proved to be a double salt of composition $[\text{NH}_4]_2[\text{Co}_6(\text{NH}_3)_{14}(\text{OH})_8(\text{O})_2][\text{ZnCl}_4]_2$. Later we redetermined the structure, this time on the other crystalline modification of the original sample, $[\text{Co}_6(\text{NH}_3)_{14}(\text{OH})_8(\text{O})_2][\text{ZnCl}_4]_2(\text{Zn}(\text{OH})_2\text{Cl}_3)_2 \cdot 2\text{H}_2\text{O}$. The latter data proved sufficiently good to successfully locate all atoms including hydrogens, an unusual circumstance for such a large molecule. The structural parameters for the cation in the three independent structural determinations are in excellent agreement, within errors, but the present structure is by far much more accurate than our previous two. The presence of both ZnCl_4^{2-} and $\text{ZnCl}_3(\text{OH}_2)^-$ counterions is clear, and in a solution containing a 6+ cation as well as NH_4^+ , Zn^{2+} , H^+ , ZnCl^+ , ZnCl_2 , Cl^- , ZnCl_3^- and ZnCl_4^{2-} , nothing surprises about what preferentially crystallises. The kinetics of crystallisation or the preferred lattice energies obviously prevail.

The ORTEP diagram is shown in Fig. 5 along with significant bond length and bond angle data. The molecular symmetry is C_{2h} , and this is almost preserved in the crystal (the inversion centre is retained, but the strict symmetry plane and C_2 axis are lost). Unlike Werner's classic hexol, this molecule is not chiral. This beautifully symmetric hexanuclear complex has two joined 'hexol' fragments which contain trivalent bridging oxygen. These are not strictly hexols, since each of the two six-donor-atom CoO_6 fragments bear two oxo rather than hydroxo donors. Trivalent oxygen centers are uncommon, but their existence is clear from the unprecedented accuracy of the present structure for which O and OH are distinguished. This same accuracy is also the reason for discerning a reduction in molecular symmetry from C_{2d} to C_s in the crystal—the structural parameters for C_2 and σ symmetry related molecular fragments are not very different, but they are different, at this level of structural accuracy (Fig. 5).

In solution, there are four distinct NH_3 environments, three of intensity 12 and one of intensity 6, as observed in the ^1H NMR spectrum (Fig. 4). In addition there are two distinct kinds of bridging OH groups, of intensity 4 each. Only one of these is observed, likely that for the tetraammine fragments; presumably the other OH protons are in exchange with trace water (a water signal is always observed, at ca. 3.4 ppm), and perhaps involving the adjacent oxo groups which could be internally protonated. The chemical shifts for the ammine signals were in accord with the structure: Co– NH_3 *trans* to bridging OH at δ 4.1 and *cis* to

bridging OH at δ 2.9, very much the same shifts as in the parent *cis*-diol dimer $[(\text{NH}_3)_4\text{Co}(\text{OH})_2\text{Co}(\text{NH}_3)_4]^{4+}$ and in Werner's original hexol. The third and fourth signals were at δ 3.5 and, of half intensity, at δ 2.95 (clearly *trans* to the oxo bridge). These are the resonances for the triol portions of the hexanuclear complex. The corresponding signal in the parent triol $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$ is observed at δ 3.1, but is split into two signals (2 : 1) either side of this in Werner's second hexol because of the presence of the central oxo groups which remove the threefold symmetry. The high field hydroxo signal at δ –2.0 (4H) has the correct integration; we used the known compounds $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$ and $[\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}\text{Co}]^{6+}$ to check that the relative integrations of the NH_3 and OH signals correctly reflected proton numbers. Finally, a 1 : 1 : 1 triplet is observed at ca. δ 7 ppm which is due to the NH_4^+ cation of the component of the di- or polymorphic mixture which contains a salt of composition $[\text{NH}_4]_2[\text{Co}_6(\text{NH}_3)_{14}(\text{OH})_8(\text{O})_2][\text{ZnCl}_4]_2$.

This remarkable hexol has both rotational and reflection symmetry and is therefore not resolvable into optical isomers. Werner's historic first hexol, the structure for which Werner recognised and which he resolved, will always remain the more significant. The existence of bridging oxo rather than hydroxo is likely the result of the high positive charge, although not the entire story because his first hexol is also 6+ and bridging hydroxo groups prevail.

We thank the Australian Research Council for financial assistance.

Notes and references

§ The 'lost' structure: crystal data: $[\text{Co}_6(\text{OH})_8(\text{O})_2(\text{NH}_3)_{14}(\text{NO}_3)_6 \cdot 4\text{H}_2\text{O}]$, $M = 1204.18$, monoclinic, $P2_1/n$, $a = 1152.3(4)$, $b = 1449.2(2)$, $c = 1166.7(2)$ pm, $\beta = 98.49(2)^\circ$, $Z = 2$, $D_c = 2.076$ Mg m^{-3} , 2285 reflections measured, 1874 with $I > 1\sigma(I)$, MoK α ($\lambda = 0.71073$ Å), anisotropic temperature factors for Co, O, and N, 253 independent parameters; $R = 0.076$, R_w ca. 0.04. H-atoms were not refined. Average bond lengths: Co–N, 287(6), Co–OH, 195(12), Co–O, 193(9), Co–O, 192(8) pm, Co–O–Co, 96.9(3) and 95.7(4) $^\circ$. CCDC 240886. See <http://www.rsc.org/suppdata/cc/b4/b408277j/> for crystallographic data in .cif format.

¶ All the complexes reported herein were synthesised by the cited literature procedures except for the hexol double salt.

|| The complex cation in this double salt has the same basic structure as found in all three determinations; the NH_4^+ ions are H-bonded to one Cl^- of a ZnCl_4^{2-} counterion, and also to an adjacent oxo bridging group.

** Crystal data: $[\text{Co}_6(\text{OH})_8(\text{O})_2(\text{NH}_3)_{14}][\text{ZnCl}_4]_2(\text{Zn}(\text{OH})_2\text{Cl}_3)_2 \cdot 2\text{H}_2\text{O}$. Dark green plate, $0.1 \times 0.2 \times 0.3$ mm, $M = 1590.00$, $T = 173$ K, triclinic, $P\bar{1}$, $a = 1042.58(5)$, $b = 1143.07(7)$, $c = 1212.34(5)$ pm, $\alpha = 114.307(7)^\circ$, $\beta = 105.416(6)^\circ$, $\gamma = 94.686(8)^\circ$, $V = 1172.79(17)$ Å 3 , $Z = 2$, $D_c = 2.251$ Mg m^{-3} , 6326 reflections measured, 4521 with $I > 3\sigma(I)$, Nonius Kappa CCD instrument, graphite monochromator, MoK α ($\lambda = 0.71073$ Å), $R = 0.0219$, R_w 0.0263. Crystal data for this last structure have been deposited at the Inorganic Crystal Structure Database as csd 414065 (see <http://icsdweb.fiz-karlsruhe.de/> for crystallographic files in .cif format).

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